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Environmental Monitoring Near Industrial Sites: Sampling & Analysis of Selected Toxic Substances. Task I-Vinylidene Chloride

Midwest Research Inst, Kansas City, Mo

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16. ABSTRACT

A sampling and analysis program was conducted to determine the levels of vinylidene chloride in air and water around six industrial sites, in selected municipal drinking waters and in selected polymeric materials. The industrial sites included monomer producers, polymer producers and polymer users.

Air was collected at perimeters of the industrial sites as 24-hr composite samples using charcoal adsorption tubes. Grab water samples were collected up- and downstream, at the plant discharge and at the municipal water treatment plants.

Air levels ranged from 52 $\mu g/m^3$ to nondetectable at the industrial sites; water levels ranged from 550 μg/liters to nondetectable at the plant sites and from 0.06 μg/liters to nondetectable in the drinking waters. The air and water samples were analyzed by GC and results confirmed by GC/MS. Other components in the samples were identified by GC/MS.

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SAMPLING AND ANALYSIS OF SELECTED TOXIC SUBSTANCES

Task I - Vinylidene Chloride

Contract No. 68-01-4115

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NOTICE

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SECTION I

SUMMARY

The purpose of this program was to provide sampling and analysis capabilities to EPA's Office of Toxic Substances, so that the levels of suspected toxic substances in air, water, soil, and sediment at designated locations throughout the United States could be determined. The first task was the sampling and analysis for vinylidene chloride (VDC).

Methods for sampling and analyzing VDC in air, water, and solids were evaluated. A protocol was developed and approved.

Six industrial plants were selected for sampling. The plants represented manufacturers of VDC monomers, manufacturers of VDC polymers, and fabricators of VDC polymers. Drinking water samples from four major U.S. cities were collected. Several types of solid final products made from VDC polymers or co-polymers were obtained from producers or purchased.

A summary of the results from the industrial plant samples is shown in Table 1. The high and low concentration of VDC in air and water samples for each plant are listed along with a description of the type of usage of VDC. In general, VDC in air was found only at monomer and polymer production facilities. The highest level detected, 51.8 $\mu g/m^3$ (0.014 ppm) was found downwind of a monomer production plant at the property line. At sites where VDC was found, its' distribution correlated with the wind behavior that existed during the sampling period. The greatest distance at which VDC was detected away from plant property was 0.6 miles. VDC was detected, however, at a station which was at a property line but known to be 1.5 miles from the VDC production facilities.

The presence of VDC in the samples was confirmed by both (a) bromination of VDC followed by gas chromatographic analysis of the resulting 1,2-dibromo-1,1-dichloroethane, and (b) gas chromatography/mass spectrometry (GC/MS) analysis of the original VDC sample.

Table 1. DATA SUMMARY FOR PROGRAM TASK 1

Site	Process	Air (μg/m³) High	Air (μg/m³) Low	Water (ug/ℓ) High	Water (ug/ℓ) Low
Dow Chemical Plaquemine, Louisiana	Producer of VDC	9.6	ND[a]	0.2	ND
PPG Industries Lake Charles, Louisiana	Producer of VDC User of VDC to produce methyl chloroform	51.8	ND	550	ND
Dixico Dallas, Texas	User of PVDC barrier coating latex	ND	ND	b/	b/
Dewey and Almy Owensboro, Kentucky	Producer of barrier coating latex	ND	ND	ND	ND
Tennessee Eastman Kingsport, Tennessee	Producer of modacrylic fibers	< 1	ND	< 1	ND
Dow Chemical Midland, Michigan	Use of VDC to produce polymers Fabricator of extrusion resins	25	ND	< 1	ND

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a/ ND = Not detected.
b/ No sample available.

The highest level of VDC in water was 550 ppb, found in an industrial wastewater canal. Generally, the level was less than 1 ppb and was detectable by GC/MS only.

Confirmation of VDC in the water samples was made by GC/MS analysis.

The results of analysis of drinking waters from four major U.S. cities are summarized in Table 2. VDC was detected only in the Miami, Florida sample. The results are confirmed since the samples were analyzed by GC/MS.

VDC was found in two samples of Saran Wrap at 4.9 and 58 ppm. No VDC was detected in PVDC monofilaments, modacrylic fibers or meat packaging film.

In the process of obtaining GC/MS confirmation of VDC in air and water samples, the identities of other compounds in those samples were established. Tables 3 and 4 summarize the compounds found in the air and water samples, respectively.

Table 2. VDC CONCENTRATIONS IN DRINKING WATER FROM FOUR U.S. CITIES

Sample	VDC ($\mu g/\ell$)
Cincinnati, Ohio	
Pre-chlorination	ND
Post-chlorination	ND
Lawrence, Massachusetts	
Pre-chlorination	ND
Post-chlorination	ND
Miami, Florida	
Pre-chlorination	0.059
Post-chlorination	0.045
Waterford, New York	
Pre-chlorination	a/
Post chlorination	a/
Philadelphia, Pennsylvania	
Pre-chlorination	ND
Post-chlorination	ND

ND = Not Detected

a/ Sample not received in time for scheduled analysis.

Table 3. SUMMARY OF ORGANIC COMPOUNDS FOUND IN AIR SAMPLES

Compound	Dow Chemical Plaquemine, Louisiana	PPG Industries Lake Charles, Louisiana	Dixico Dallas, Texas	Dewey and Almy Owensboro, Kentucky	Tennessee Eastman Kingsport, Tennessee	Dow Chemical Midland, Michigan
Vinylidene chloride	X	X			X	X
trans-Dichloroethylene						X
Hexanes					X	X
Cyclohexane or hexene					X	
Methylene chloride						X
Carbon tetrachloride	X	X			X	
cis-Dichloroethylene		X				
Chloroform	X	X				
Trichloroethylene	X	X				
C-6 Methyl ketones					X	
Methyl chloroform		X				X
Benzene	X	X			X	X
Tetrachloroethylene	X	X				
Toluene	X				X	X
1,1,2-Trichloroethane		X				
1,2-Dichloropropane	X					

Table 4. SUMMARY OF ORGANIC COMPOUNDS FOUND IN WATER SAMPLES

Compound	Dow Chemical Plaquemine, Louisiana	PPG Industries Lake Charles, Louisiana	Dixico Dallas, Texas	Dewey and Almy Owensboro, Kentucky	Tennessee Eastman Kingsport, Tennessee	Dow Chemical Midland, Michigan	Drinking waters
Methylene chloride	X					X	
Vinylidene chloride	X	X			X	X	X
Dimethoxymethane						X	
Chlorobromomethane						X	
trans-Dichloroethylene	X	X				X	
cis-Dichloroethylene	X	X					
Chloroform	X	X				X	
Ethylene dichloride	X	X				X	
Dibromomethane						X	
Methyl chloroform	X	X					
Carbon tetrachloride	X					X	
1,2-Dichloropropane	X						
Benzene	X					X	
Trichloroethylene	X	X				X	
1-Chloro-3-bromopropane						X	
1,1,2-Trichloroethane	X	X					
Methyl cyclohexane	X						
Bromoform		X					
Tetrachloroethylene	X	X				X	
Toluene	X						

SECTION II

INTRODUCTION

A concern about the environmental exposure to vinylidene chloride (VDC) has developed recently, stimulated at least partially by its structural similarly to vinyl chloride and trichloroethylene, both carcinogens. Studies of the carcinogenicity of VDC with test animals, however, have been contradictory and controversial. No clear understanding of its threat to the environment is available at this time. It is also not known to what extent the general population is being exposed to VDC.

On July 29, 1976, MRI Project No. 4280-C(1) entitled "Sampling and Analysis of Selected Toxic Substances" was initiated. The objective of this program was to provide the EPA with sampling and analysis capability to determine the level of toxic substances in air, water, soil, and sediment from designated sources and ambient locations throughout the United States. The first task on this program was the sampling and analysis for VDC.

This report describes Task I of the program as follows: Section III, Experimental Methods; Section IV, Site Selection; and Section V, Discussion of Results.

SECTION III

EXPERIMENTAL METHODS

SAMPLING PROTOCOL

Air Sampling

Air was sampled at 7 to 13 stations deployed around the industrial sites. Meteorological data obtained from the National Climatic Center was used to establish the most probable ind patterns for the time of sampling. A small array of sites (three to five) was established at the property line at an upwind, a downwind and two crosswind points. The remaining stations were positioned in an array upwind and downwind, with most of the stations being downwind. If possible, the downwind sampling stations were positioned such that samples were collected at the property line and at a minimum of two different distances from the property line. The sampling probes were set at 4 to 6 ft above ground at all stations and air was sampled continuously for 24 hr.

The meteorological conditions that existed during each test obtained from the nearest National Weather Station. Wind speed and direction, temperature and precipation data were included in the data log.

The sampling train for the collection of VDC from ambient air consisted of the following components assembled in the order given: (a) probe (directed into the wind); (b) top charcoal tube; (c) back-up charcoal tube; (d) critical orifice; and (e) 24-v DC vacuum pump.

The charcoal tubes were constructed of glass and were 8 mm OD x 6 mm ID x 18 cm in length. They were packed with approximately 1.8 g 6/14 mesh Fisher charcoal that was activated at 400°C for 1 hr under a stream of nitrogen. Minimum lengths of natural rubber tubing were used to connect the sampling tubes to the pump. Flow was maintained at 0.5 or 1 liter/min by using a hypodermic syringe needle as a critical orifice and was checked in the field every 3 to 4 hr. Power was supplied to the DC pump by two 24-v lantern batteries connected in parallel. The pump and batteries were encased in a cardboard-polystyrene shipping box which was then anchored at the sampling site. The reliability of this system has been demonstrated in previous OTS studies.[1/] After sampling was completed, the tubes were capped with rubber slip-on septa, wrapped in aluminum foil and stored over dry ice for shipment to MRI. At MRI, the tubes were kept on dry ice until analyzed.

Water Sampling

Water samples were collected in 25 ml glass screw-top vials fitted with caps lined with Teflon®-rubber laminate discs (Teflon® side down) obtained from Pierce Chemical Company. All water samples were grab samples. The vials were filled with a water sample to overflowing and then immediately sealed with the septa cap with no headspace. As the samples were taken, they were placed on ice and then kept at ice temperature (4 to 6°C) until they were analyzed.

Consumer Product Sampling

The consumer products that were analyzed for residual monomer were obtained from the manufacturer or purchased directly at a retail outlet.

ANALYSIS PROTOCOL

Air Samples

Exactly 4 ml of reagent grade CS_2 was placed in a 7-ml vial filled with a Teflon®-faced septum and cooled on dry ice. The charcoal from the adsorption tubes was slowly added to the CS_2 with gentle swirling. After all the charcoal has been added, the cap was replaced and the vial shaken periodically. The desorption of the VDC from the charcoal was allowed to proceed for at least 45 min. The VDC was analyzed by GC with flame ionization detection using the conditions listed in Table 5 as AIR-PRIMARY.

For GC confirmation of identity, 1.0 ml of the CS_2 solution was placed in a 3.5 ml vial. An approximately 500-fold molar excess of Br_2 was added based upon the analytical results obtained in the primary analysis. After 30 min, the excess Br_2 was removed by two extractions with an equal volume of 0.5 M NaOH. The CS_2 was dried by passage through a microcolumn of Na_2SO_4 and diluted to 1.0 ml if necessary. Analysis for brominated VDC was performed by GC using the conditions listed in Table 5 as AIR-CONFIRMATION.

Additional confirmation was obtained by GC/MS operated under the following conditions using the AIR-PRIMARY column.

Table 5. GAS CHROMATOGRAPHIC CONDITIONS FOR VDC ANALYSIS

Sample	Column	Column temperature	Carrier flow	Species analyzed
AIR-PRIMARY	6 ft x 4 mm glass packed with Durapak OPN on 80/100 Porasil C	60°C for 2.0 min, 20°/min to 120°C. Hold 10 min	Nitrogen at 38 ml/min (Helium at 30 ml/min for GC/MS)	VDC
AIR-CONFIRMATION	6 ft x 1/8 in. stainless steel packed with 1.5% OV-101 on 80/100 Chromosorb W	90°C	Nitrogen at 38 ml/min	BR VDC
WATER-PRIMARY	6 ft x 1/8 in. stainless steel packed with 0.2% Carbowax 1500 on Carbosieve C	60°C for 3.0 min, then 10°/min to 140°C. Hold 5 min	Nitrogen at 40 ml/min	VDC
WATER-CONFIRMATION (GC/MS)	6 ft x 1/8 in. stainless steel packed with 0.2% Carbowax 1500 on Carbosieve C	60°C for 3.0 min, then 10°/min to 140°C. Hold 5	Helium at 30 ml/min	VDC
SOLIDS-PRIMARY	6 ft x 4 mm glass packed with Durapak OPN on 80/100 Porasil C	90°C	Nitrogen at 38 ml/min	VDC

Instrument: Varian MAT 311A Mass Spectrometer/Varian 2700 Gas Chromatograph
Data System: Varian Spectro System 100 MS
Separator: Watson/Bieman
Ionization Potential: 70 ev
Emission Current: 1 milliamp
Multiplier Gain: 10^7
Mass Range: 45-200
Scan Rate: 5.5 sec/decade
Resolution: 1,000
Sampling Rate: 6 KH_z

Water Samples

The water samples were analyzed by the purge and trap technique. The purging apparatus consisted of a 35 mm x 8 mm ID glass column (Glenco, Inc.) fitted with a fine glass frit at the bottom and a Teflon® compression union with Teflon® rings at the top that held the Tenax-GC®-packed tube. A stream of prepurified nitrogen further purified by a charcoal trap was employed at the rate of 38 ml/min to purge the water samples. A 3 in. x 1/4 in. stainless steel tube packed with 60/80 mesh Tenax-GC® (Applied Science Laboratories, Inc.) was used to trap VDC purged from water. The water sample was poured into the back of a 10 ml glass syringe (American Hospital Supply Corporation) to overflowing, the plunger was then replaced and pushed to the 5 or 10 ml level. This technique was used to avoid a headspace in the syringe. The sample was introduced from the syringe into the top of the VOA column, minus the Tenax® tube, and the plunger forced down. The Tenax® tube was replaced immediately and left in the system for 10 min. The packed tube was removed from the VOA apparatus and put into the Bendix flasher oven where it was immediately thermally desorbed onto the GC column. VDC was analyzed by a flame ionization detector using the column and conditions listed in Table 5 as WATER-PRIMARY.

Samples were confirmed by GC/MS using the same column described under WATER-CONFIRMATION. The operation conditions when full mass spectra were collected were as follows:

Instrument: Varian MAT 311A Mass Spectrometer/Varian 2700 Gas Chromatograph
Data System: Varian Spectro System 100 MS
Separator: Watson/B
Ionization Potential: 70 ev
Emission Current: 1 milliamp
Multiplier Gain: 10^7
Mass Range: 45-200
Scan Rate: 5.5 sec/decade
Resolution: 1,000
Sampling Rate: 6 KH_z

Some samples were analyzed by the same instrumentation but operated in the Multiple Ion Scan (MIS) mode. The four most intense peaks in the mass spectrum of VDC, 61, 96, 98, and 63, were monitored.

Solid Samples

A known weight (1 to 5 g) of the solid was placed in a crimp-seal vial and sealed. The vial was heated to 100°C and held there for 90 min. A 100-μl sample of headspace was analyzed for VDC by GC using the condition listed in Table 5 as SOLIDS-PRIMARY. The samples were analyzed in triplicate if sufficient material was available.

METHOD DEVELOPMENT FOR SAMPLING AND ANALYSIS

A meeting was held on August 31, 1976, at Cincinnati EPA laboratories for the purpose of discussing the proposed sampling and analysis program for VDC. The following were in attendance.

Andrew E. O'Keeffe	Environmental Monitoring Support Laboratory, Research Triangle Park (EMSL-RTP)
Hal Richter	Office of Air Quality and Pollution Standards, Research Triangle Park (OAQPS-RTP)
John Margeson	Quality Assurance Branch, Environmental Monitoring Support Laboratory, Research Triangle Park (QAB-EMSL-RTP)
John Going	Midwest Research Institute (MRI)
Perry Brunner	Office of Toxic Substances (OTS)
Thomas A. Bellar	Environmental Monitoring Support Laboratory, Cincinnati (EMSL-CIN)
Jim Lichtenberg	Environmental Monitoring Support Laboratory, Cincinnati (EMSL-CIN)
John G. Cobler	Dow Chemical, Midland, Michigan
William A. Coniglio	Office of Toxic Substances (OTS)

After extensive discussion of alternate sampling and analysis procedures the following items were a consensus of the group:

* The optimum air sampling material was expected to be activated charcoal with carbon disulfide as a desorbing solvent.

* An electron capture detector was reported by Mr. Cobler, of Dow Chemical, as being more sensitive than a flame ionization detector and was used by Dow Chemical. In a subsequent phone conversation, Mr. Cobler stated that in fact the electron capture detector was incompatible with carbon disulfide and that a FID was actually used.

- Mr. Cobler stated that VDC could be separated from carbon disulfide by GC using a Durapak OPN column. No significant interferences were reported.

- The problem of maintaining quality control was discussed. The possibility of obtaining charcoal tubes loaded with a known amount of VDC to be used as quality control checks was suggested.

- A protocol for the sampling and analysis ofVVDC in water was presented by Mr. Tom Bellar, EMSL-CIN. The procedure uses a generally accepted approach for the analysis of volatile organics in water samples. The preference to conduct continuous sampling rather than discrete grab sampling, as in the VOA technique, was stated by Dr. Coniglio. The possibility of using charcoal for continuous water sampling will be investigated.

- The importance of verification of compound identification was emphasized. Identification by two columns and/or two detectors was considered as the minimum verification required. However, confirmation by gas chromatography/mass spectrometry (GC/MS) was the preferred technique.

Gas Chromatographic Conditions

Carbon Disulfide Extracts of VDC - As a result of the project meeting on August 31, 1976, in Cincinnati, it was assumed that VDC collected in air samples would most likely be analyzed in a carbon disulfide solution. Thus, the initial and major analytical problem would be the gas chromatographic separation of VDC and the solvent. A series of columns were tested using flame ionization detection for their ability to retard either VDC or carbon disulfide. A 12-ft column packed with 10% SP-2100 on 100/120 Supelcoport showed marginal success. At a column temperature of 30°C, VDC eluted approximately 0.1 to 0.2 min ahead of the solvent. It was observed that the actual retention time of VDC decreased as the volume of sample injected was increased. Furthermore, the peak shape was very dependent upon the injection technique and varied with operators. Ultimately, this column was judged to be unacceptable.

A 6 ft x 4 mm glass column packed with 80/100 mesh Durapak OPN on Porasil C was then found to be satisfactory. The following conditions were found to be optimum for separation of VDC from the solvent and other chlorinated hydrocarbons.

Columns: Dual 6 ft x 4 mm glass packed with 80/100 mesh Durapak OPN on Porasil C

Detectors: Dual hydrogen flame ionization operated in differential mode

Carrier: Nitrogen at 30 ml/min

Column Temperature: 60°C for 2.0 min then programmed at 10°C/min to 100°C and held at 100°C for 5 min

Injector Temperature: 200°C

Detector Temperature: 275°C

The chromatographic behavior of 14 chlorinated hydrocarbons, 2-propanone and diethyl ether was determined. The absolute retention times and retention times relative to VDC are listed in Table 6.

A chromatogram showing the elution peaks of most the compounds is shown in Figure 1. Methyl chloride, vinyl chloride, 2-propanone, and diethyl ether were omitted from the mixed standard since they all co-elute with carbon disulfide. The only compound which would seriously interfere is chloroethane. This was not expected to cause any serious problems except at the PPG monomer production facility at Lake Charles, Louisiana. PPG produces chloroethane at this plant at the rate of 120 million pounds per year.

A stock solution of VDC was prepared by injecting 199 µl of VDC into 10 ml of CS_2 at 0°C. The resulting 5.0 ppt solution was stored in a freezer held at -13°C. Working standards were prepared daily by injecting a known volume of the stock standard into a small volume of CS_2 in a septum sealed vial. A calibration curve of VDC in CS_2 was prepared using the conditions previously described. A plot of peak area versus nanograms VDC, shown in Figure 2 was linear from 13 to 550 ng. The detection limit was about 10 ng.

Brominated Carbon Disulfide Extracts of VDC - Samples of VDC in carbon disulfide were brominated as a means of confirming VDC identity. The principal purpose of the bromination procedure was to establish whether a GC peak on the Durapak OPN column was due to the presence of VDC or chloroethane. Chloroethane had been shown to coelute with VDC on the Durapak OPN column and could interfere with the analysis. Thus, the behavior of chloroethane during the bromination was studied. The behavior of the chlorinated alkenes, *cis*-dichloroethene, *trans*-dichloroethene, and trichloroethene was also established. It was determined that a 6 ft x 1/8 in. stainless steel column of 1.5% OV-101 on Chromosorb W at 90°C could be used to separate brominated VDC from CS_2.

Table 6. RETENTION TIMES ON DURAPAK OPN COLUMN

Compound	t_R[a] (min)	$\frac{t_R}{t_{R,\ VDC}}$
Chloroethane	2.28	0.53
Chloroethene	2.50	0.58
2-Propanone	3.10	0.72
Diethyl ether	3.70	0.86
1,1-Dichloroethene	4.33	-
Chloroethane	4.33	1.00
trans-1,2-Dichloroethene	5.13	1.18
Dichloromethane	5.63	1.30
Tetrachloromethane	6.57	1.52
cis-1,2-Dichloroethene	7.17	1.66
Trichloromethane	7.42	1.71
1,1-Dichloroethane	7.42	1.71
1,1,2-Trichloroethene	7.77	1.79
1,1,1-Trichloroethane	8.13	1.88
1,1,2,2-Tetrachloroethene	9.35	2.16
1,2-Dichloroethane	10.28	2.37
1,1,2-Trichloroethane	18.2	4.20

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[a] Chromatographic columns and conditions: Dual 6 ft x 4 mm glass columns packed with Durapak OPN on Porasil C, 80/100 mesh; column held at 60°C for 2 min, then programmed to 100°C at 20°C/min.

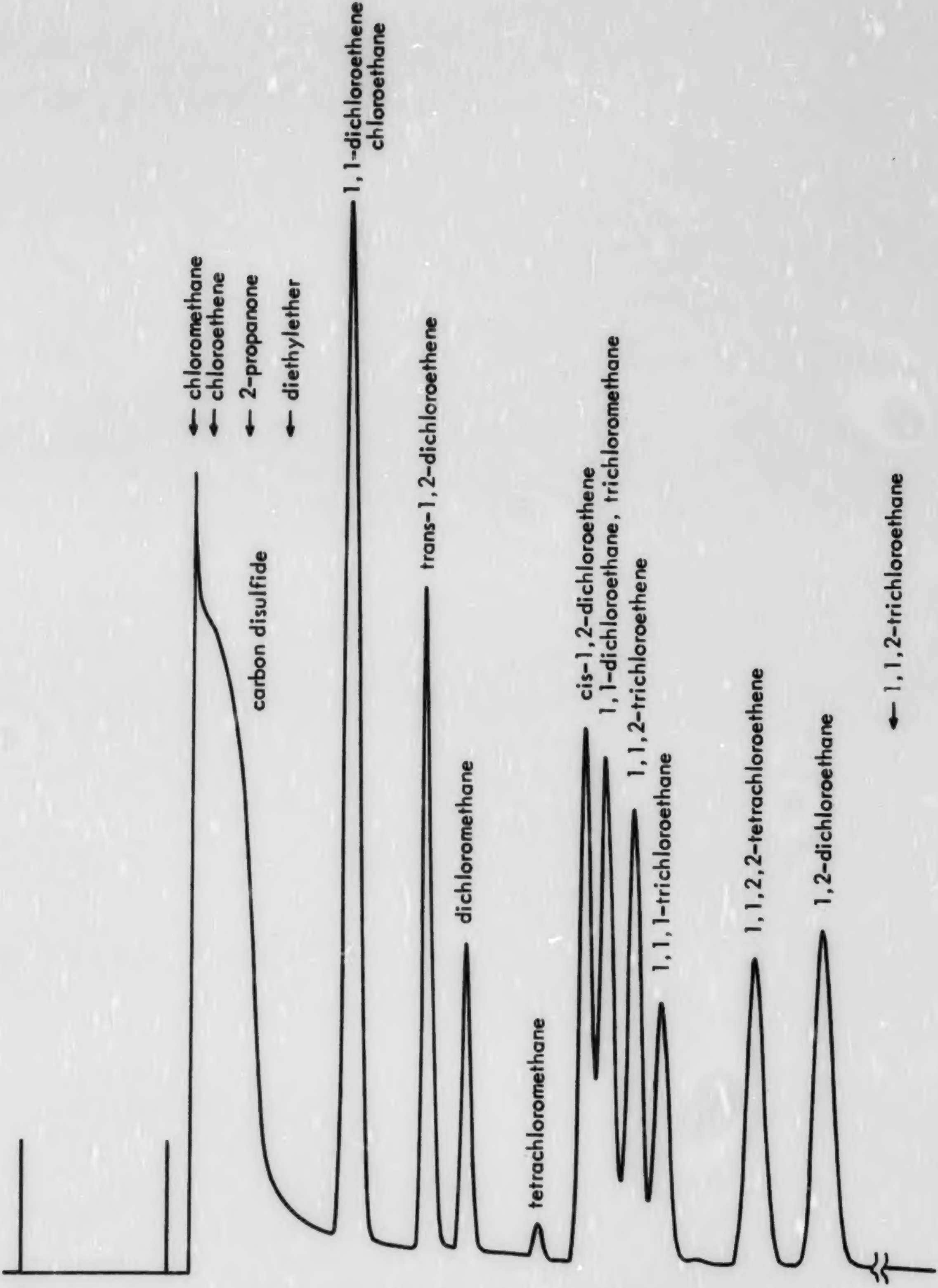

Figure 1. Chromatogram of vinylidene chloride and selected hydrocarbons

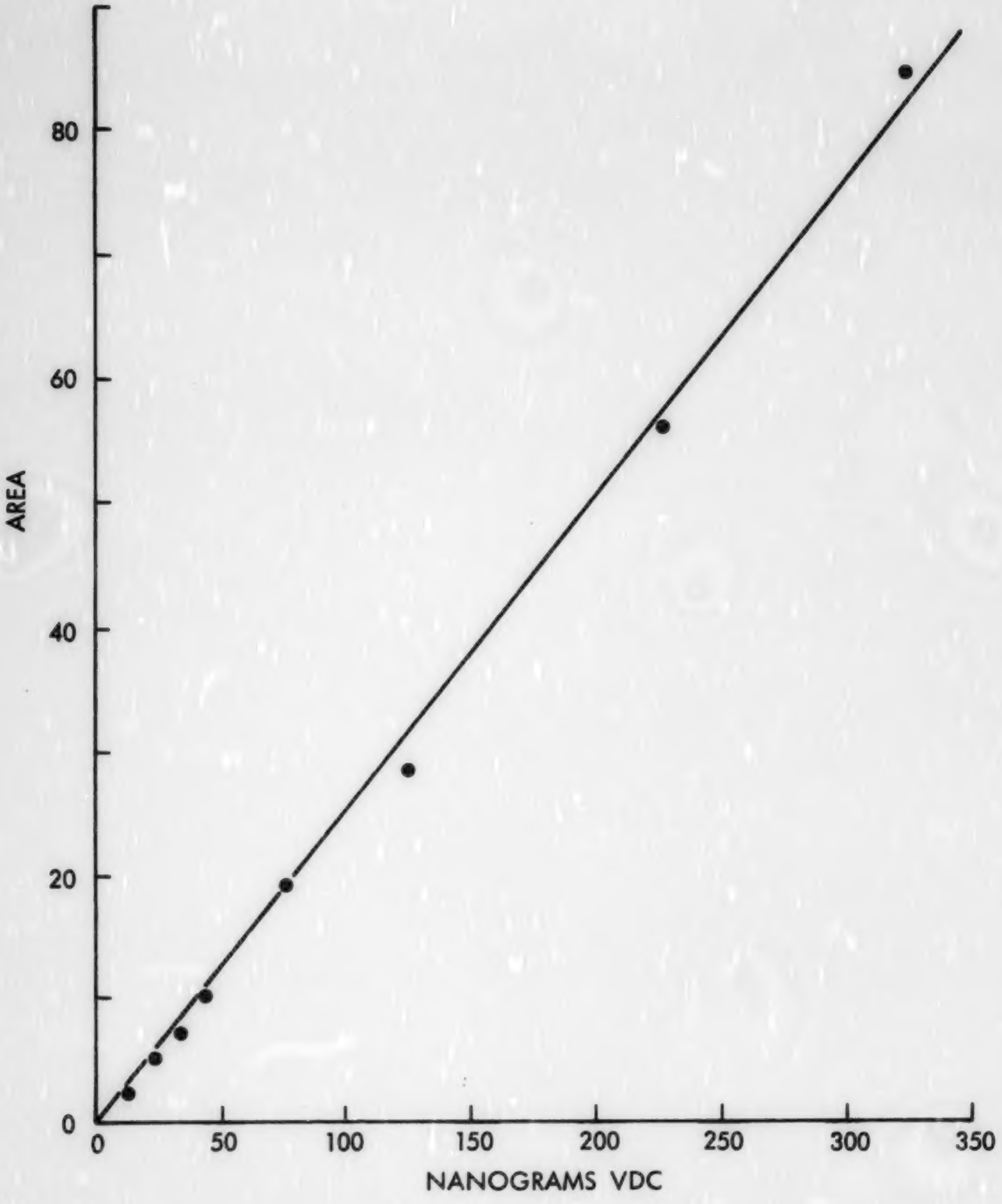

Figure 2. Calibration curve for vinylidene chloride

A mixture of VDC and chloroethane in CS_2 was brominated by an established procedure discussed later. Chromatograms of the unbrominated and brominated solutions on the OV-101 column are shown in Figure 3. VDC and chloroethane were not eluted from the OV-101 column. After bromination, the 1,2-dibromo-1,1-dichloroethane peak appeared on the OV-101 column. Experiments run with the individual compounds confirm these conclusions. As a further test, a mixture of 12 chlorinated hydrocarbons was brominated. The chromatograms are shown in Figure 4. No peaks prior to bromination were present on the OV-101 chromatogram. After bromination, the VDC, dichloroethenes and the trichloroethene peaks diminished or disappeared on the OPN column and appeared as noted on the OV-101 column. These peaks were identified by experiments run with the individual alkenes.

The cis- and trans-dichloroethenes and the trichloroethene were not completely brominated. This was not unexpected in that the bromination conditions were not optimized for these compounds. Tetrachloroethene did not appear to be brominated.

Although the bromination scheme was not intended as a means of quantitation, a calibration curve was prepared to show that the percent of bromination was constant. Two-milliliter samples ranging from 5 to 1,000 ppm VDC were brominated as prescribed and chromatographed on the OV-101 column. A graph of peak height versus ppm VDC was linear. A sample of pure 1,2-dibromo-1,1-dichloroethane could not be obtained to establish the actual percent conversion; however, the fact that all the VDC disappears on bromination indicates that the conversion is quantitative.

The brominated VDC was also chromatographed on a second column which could be used for further confirmation. The separation of the 12 chlorinated hydrocarbons, after bromination, was performed using a 10 ft x 1/8 in. stainless steel column packed with 10% SP-2100 on 80/100 mesh Supelcoport. The column temperature was 140°C and the nitrogen carrier flow was 38 ml/min. As before, only the brominated di- and tri-chloroethenes were separated from the solvent on this column.

Water Samples of VDC - The chromatographic conditions suggested by T. Bellar were modified for use at MRI. A Varian Aerograph® 2400 gas chromatographic equipped with a hydrogen flame ionization detector and a Bendix flasher connected directly to the column inlet was used for the analysis. A 6 ft x 1/8 in. stainless steel column packed with 0.2% Carbowax 1500 on 80/100 mesh Carbopack C (Supelco, Inc.) was used under the following conditions as the primary column.

Carrier: Prepurified nitrogen at 40 ml/min
Column Temperature: 60°C for 3 min, then programmed at 10°C/min to 140°C and held 5 min at 140°C
Detector Temperature: 245°C

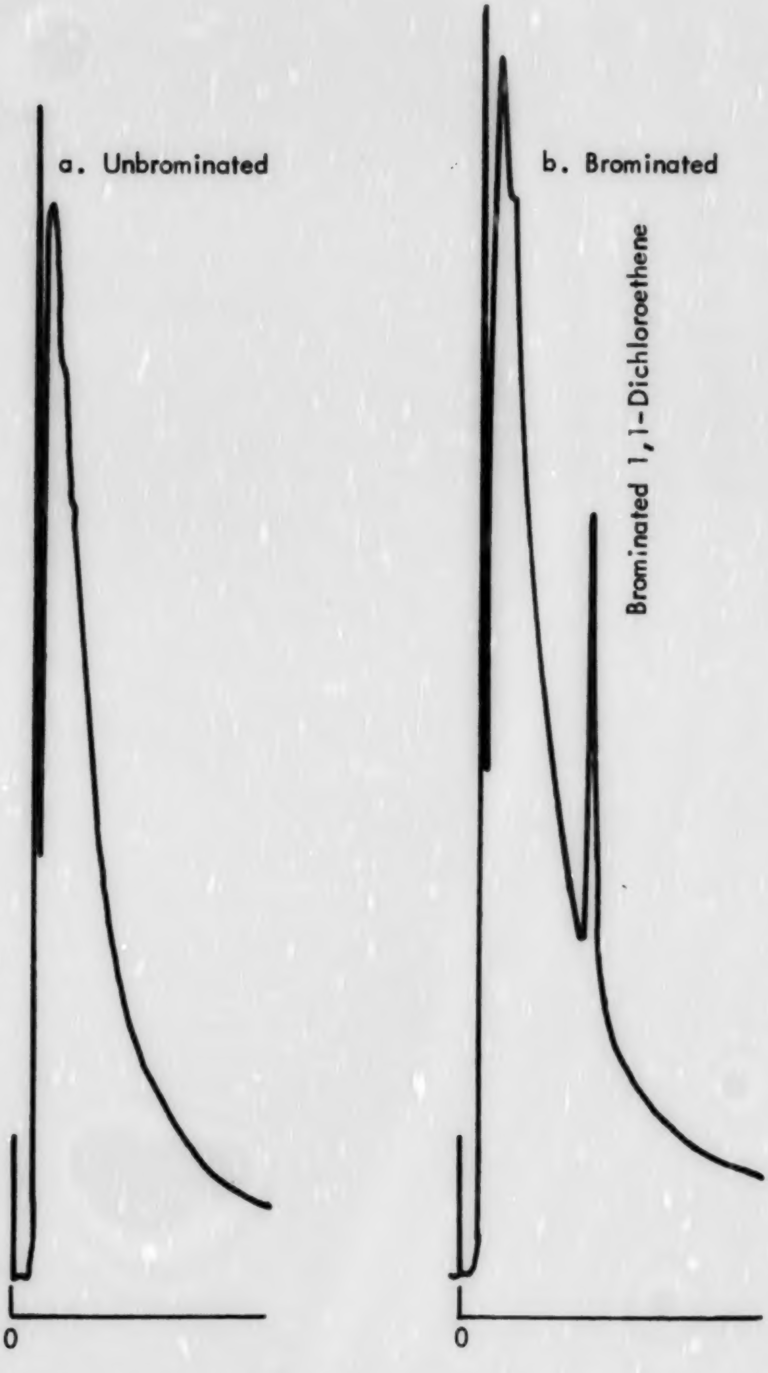

Figure 3. Chromatograms of unbrominated and brominated vinylidene chloride and chloroethane OV-101 column

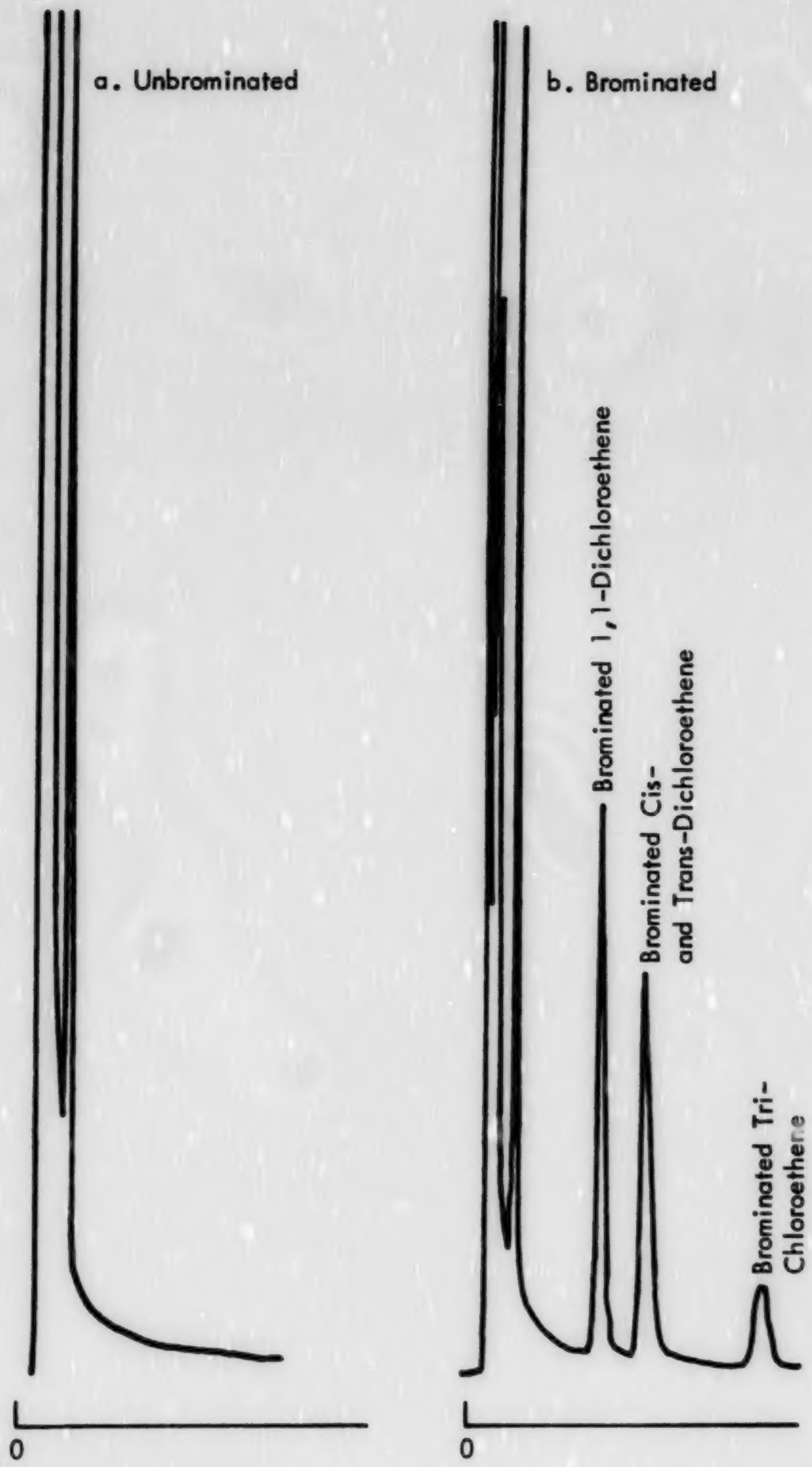

Figure 4. Chromatograms before and after bromination of 12 chlorinated hydrocarbons on OV-101 column

The chromatographic behavior of nine chlorinated hydrocarbons, 2-propanone, and diethyl ether plus VDC was determined. These 11 compounds were studied as possible interferents in the VDC analysis. The absolute retention times and retention times relative to VDC are listed in Table 7. A chromatogram showing the elution peaks of these 11 compounds and VDC is shown in Figure 5. Chloromethane and chloroethane were not run on the VOA system but had been directly injected onto the column previously and were found to have retention times shorter than VDC.

Air Samples

Desorption Studies - Since it was established in the meeting at Cincinnati that charcoal was the most promising trapping medium, this material was used in all the air sampling experiments. The two charcoals evaluated were Fisher coconut charcoal, 6/14 mesh; and Pittsburgh PCB, 12 x 30. Both were activated and cleaned at 400°C for 1 hr in a stream of nitrogen.

The optimum conditions for desorption of VDC from charcoal were studied briefly. Tubes containing 0.75 g charcoal were loaded by injecting 15 µl of 5 ppt VDC in CS_2 into a stream of nitrogen flowing through the tubes. The VDC was desorbed with 1.5 ml CS_2 at room temperature and at dry ice temperature for 30 min. The percent recovery of VDC from each charcoal at the two temperatures is summarized below.

	% Recovery	
	30°C	-78°C
Fisher	99	104
Pittsburg	108	104

Furthermore, the percent recovery of VDC was constant for both charcoals at both temperatures from 15 to 90 min desorption time. As a precaution, however, desorption will be performed at dry ice temperature for at least 45 min.

Elution Volume and Breakthrough Studies - A series of laboratory experiments were conducted to test the elution volume of the charcoal adsorption tubes. Charcoal tubes were loaded as before except that the nitrogen flowing through the tubes was continued from 1 to 6 hr at flow rates varying from 0.2 to 1 liter/min. The VDC was then desorbed as described above and the percent recovery determined. The results are summarized in Table 8.

Although the recoveries using the Pittsburg charcoal were slightly higher, no significant difference was observed between the two. It was decided to use the Fisher charcoal for future studies due to its easy availability.

Table 7. RETENTION TIMES ON CARBOWAX 1500 COLUMN

Compound	t_R [a/] (min)	t_R/t_R (VDC)
Chloroethene	1.7	0.39
Dichloromethane	3.2	0.74
2-Propanone	3.6	0.83
1,1-Dichloroethene	4.35	1.00
1,1-Dichloroethane	5.65	1.30
trans-1,2-Dichloroethene	5.65	1.30
Diethyl ether	5.9	1.36
cis-1,2-Dichloroethene	6.4	1.47
Trichloromethane	6.95	1.60
1,2-Dichloroethane	7.35	1.69
1,1,1-Trichloroethane	8.3	1.91
Tetrachloromethane	8.4	1.93

[a/] Chromatographic column and conditions: 6 ft x 1/8 in. stainless steel column packed with 0.2% Carbowax 1500 on Carbopack C, 80/100 mesh; column held at 60°C for 3 min, then programmed ato 140°C at 10 C/min.

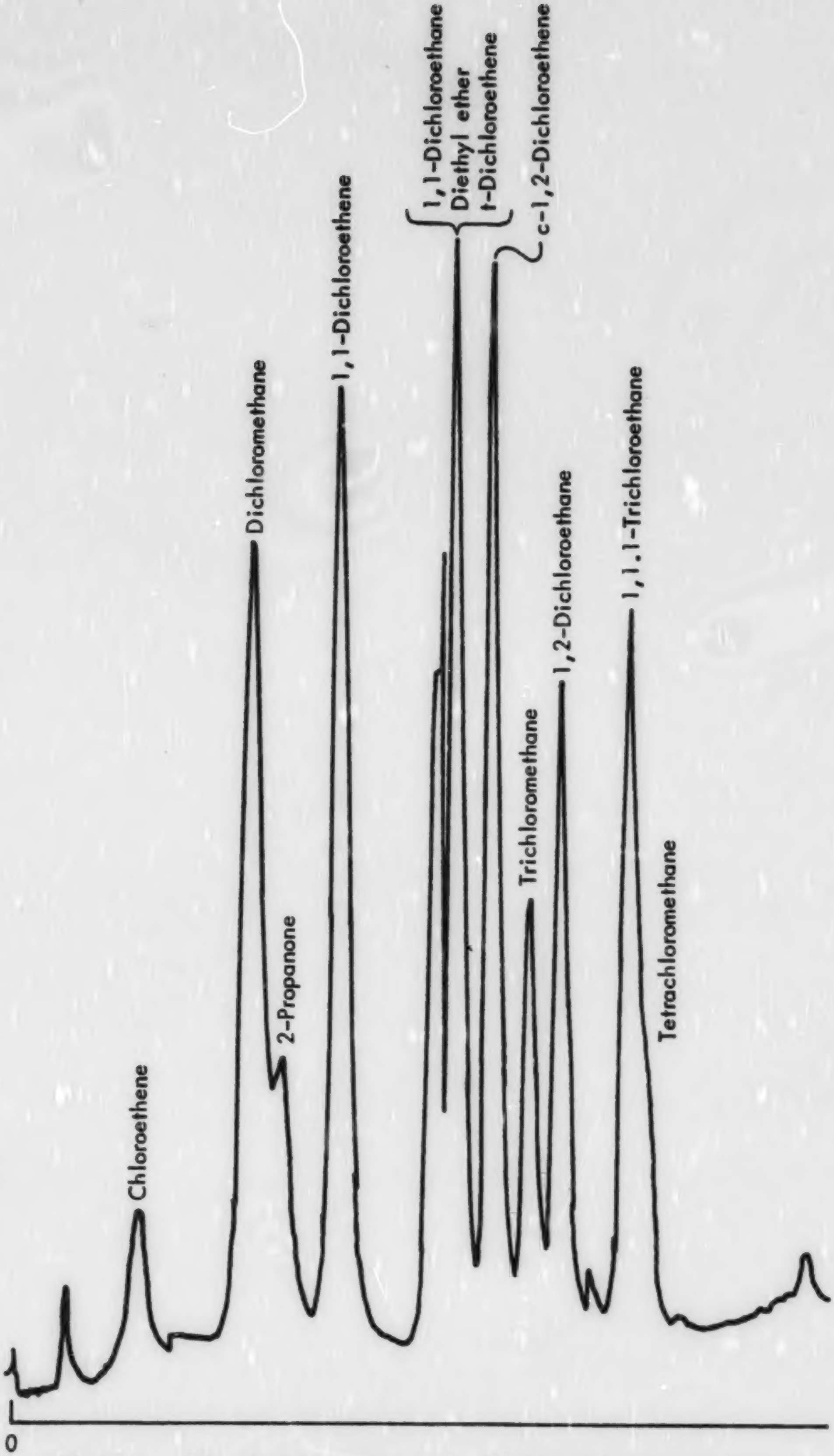

Figure 5. VOA chromatogram of 12 chlorinated hydrocarbons on Carbowax 1500 column

Table 8. LABORATORY RECOVERY STUDIES OF VDC ON CHARCOAL

	% Recovery	
Nitrogen flow	Fisher	Pittsburg
0.2 liter/min, 1 hr	96	109
0.5 liter/min, 1 hr	89	104
1.0 liter/min, 1 hr	93	102
1.0 liter/min, 6 hr	91	95

Extensive breakthrough experiments were then conducted using an inhalation chamber at the MRI Deramus Field Station. An empty chamber was operated with an atmosphere of approximately 15 ppm (v/v) VDC. The air in the chamber was drawn from outside the building and passed through the chamber at approximately 650 liters/min. Air was sampled through a port in the side of the chamber using the train shown in Figure 6.

Sampling rates of 0.13, 0.20, 0.48, and 1.0 liters/min were used. The adsorption tubes were packed with 2 g of charcoal and air was drawn through them continuously for 24 hr. After 8 and 15 hr, the lower tubes were replaced with fresh tubes for the first three experiments. All tubes were then desorbed with CS_2 and analyzed for VDC. The lower tubes were analyzed to determine the time and extent of breakthrough. The analysis conditions were such that 10 μg in any of the lower tubes would be readily detected. The results are summarized in Table 9.

At a sampling rate of 1 liter/min, a breakthrough of 37% occurred after sampling 21 ppm VDC for 23.0 hr. No breakthrough had occurred at 0.48, 0.25, and 0.18 liter/min. The percent loading (wt/wt) of the top and bottom tubes at 1 liter/min and for the top tube at 0.48 liter/min was 3.6, 2.1, and 2.5%, respectively. The maximum loading before breakthrough occurs appears to be approximately 2.5%. Sampling performed where the VDC level is suspected to be greater than 10 ppm (v/v) should be done at 0.48 liter/min. Sampling at sites where the VDC level is expected to be much lower may be done at 1 liter/min in order to collect a larger sample. Air at 10 ppb (v/v) sampled for 24 hr at 1 liter/min would provide approximately 60 μg VDC for analysis. This quantity of VDC desorbed with 4 ml of CS_2 would be easily determined by the GC analysis procedure.

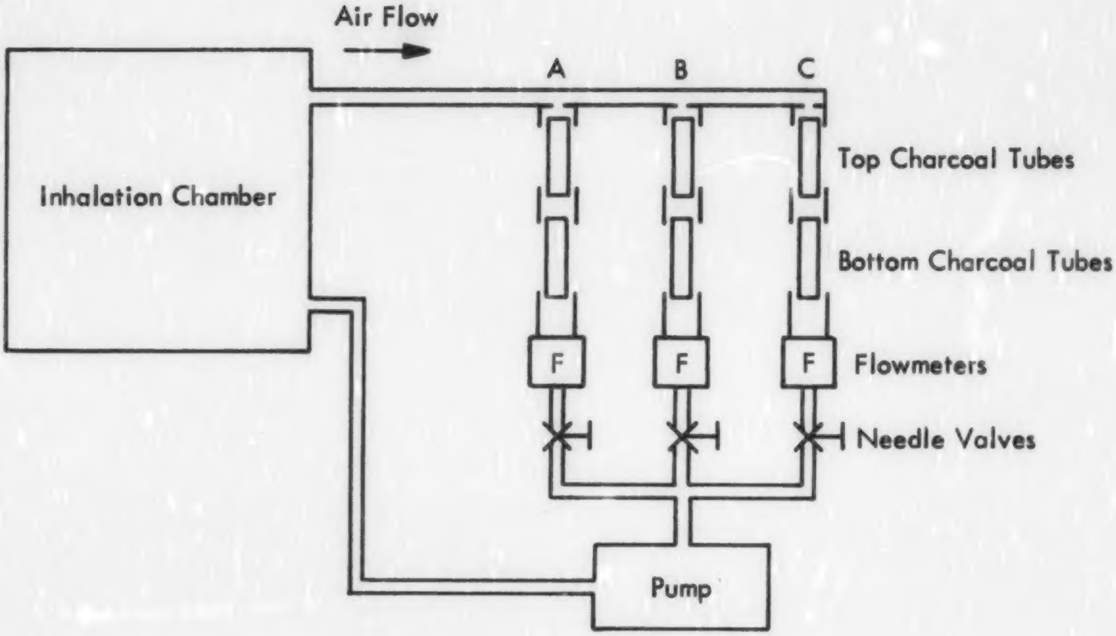
Air Flow
A
B
C
Inhalation Chamber
Top Charcoal Tubes
Bottom Charcoal Tubes
F
F
F
Flowmeters
Needle Valves
Pump

Figure 6. Sampling Train

Table 9. FIELD SAMPLING BREAKTHROUGH STUDIES[a]

Tube	Flow rate (ℓ/min)	Volume of Air (ℓ)	VDC found (mg)	ug/ℓ	ppm (v/v)
Top	0.18	250	18.9	75.6	19.2
Bottom, 0-8 hr			ND	-	-
Bottom, 8-15 hr			ND	-	-
Bottom, 15-23.5 hr			ND	-	-
Top	0.25	367	30.3	82.6	20.8
Bottom, 0-8 hr			ND	-	-
Bottom, 8-15 hr			ND	-	-
Bottom, 15-23.5 hr			ND	-	-
Top	0.48	677	49.3	72.8	18.4
Bottom, 0-8 hr			ND	-	-
Bottom, 8-15 hr			ND	-	-
Bottom, 15-23.5 hr			ND	-	-
Top	1.00	1,380	71.2	81.8	20.7
Bottom, 0-23 hr	1.00		41.7		

Note: ND = Not detected.

[a] Air temperature - 70 to 72°F.
Humidity - 39 to 42%.

Recovery at Various Loading Levels (Collected from Air) - An experiment was performed to determine the percent recovery at various levels of loading. Since the real VDC level in the chamber was not known at the time, the volume of air sampled was recorded. The volume ranged from 0.5 to 100 liters. The amount of VDC collected was determined and is listed in Table 10 along with the volume of air sampled. These data are also graphed in a log-log form in Figure 7. The three data points from the breakthrough experiment have been added to the graph although these samples were collected with a different sampling train over a longer time period. The fact that a linear curve is observed is evidence that the percent recovery was essentially constant over the range of 35 to 49,300 µg VDC. Previous experiments had also indicated that recovery was essentially complete.

Table 10. VDC COLLECTED

Volume of air sampled (ℓ)	VDC found (µg)
0.50	35
1.25	83
2.50	134
12.5	960
25.0	1,670
100	5,400

VDC Stability on Charcoal - The final experiment was designed to establish how long VDC trapped on charcoal is stable. Sixteen tubes were loaded at the inhalation chamber with 3.00 liters of air each. After loading, the tubes were plugged with corks, wrapped in aluminum foil, and stored in a freezer at 4°C. The results of duplicate samples analyzed periodically for up to 16 days after preparation are listed in Table 11. The recovery was constant for up to 16 days of storage.

VDC Stability in CS_2 - The stability of dilute solutions of VDC in CS_2 was determined. Three standards, each containing 100 ppm VDC and 1,1-dichloroethane (DCEA) were prepared and stored in a freezer, a refrigerator, and at room temperature. DCEA was added as an internal standard. The solutions were analyzed over a period of 7 days and compared to a comparable standard prepared fresh daily. The results are plotted in Figure 8 as the ratio of the areas of VDC and DCEA and as the parts per million VDC found.

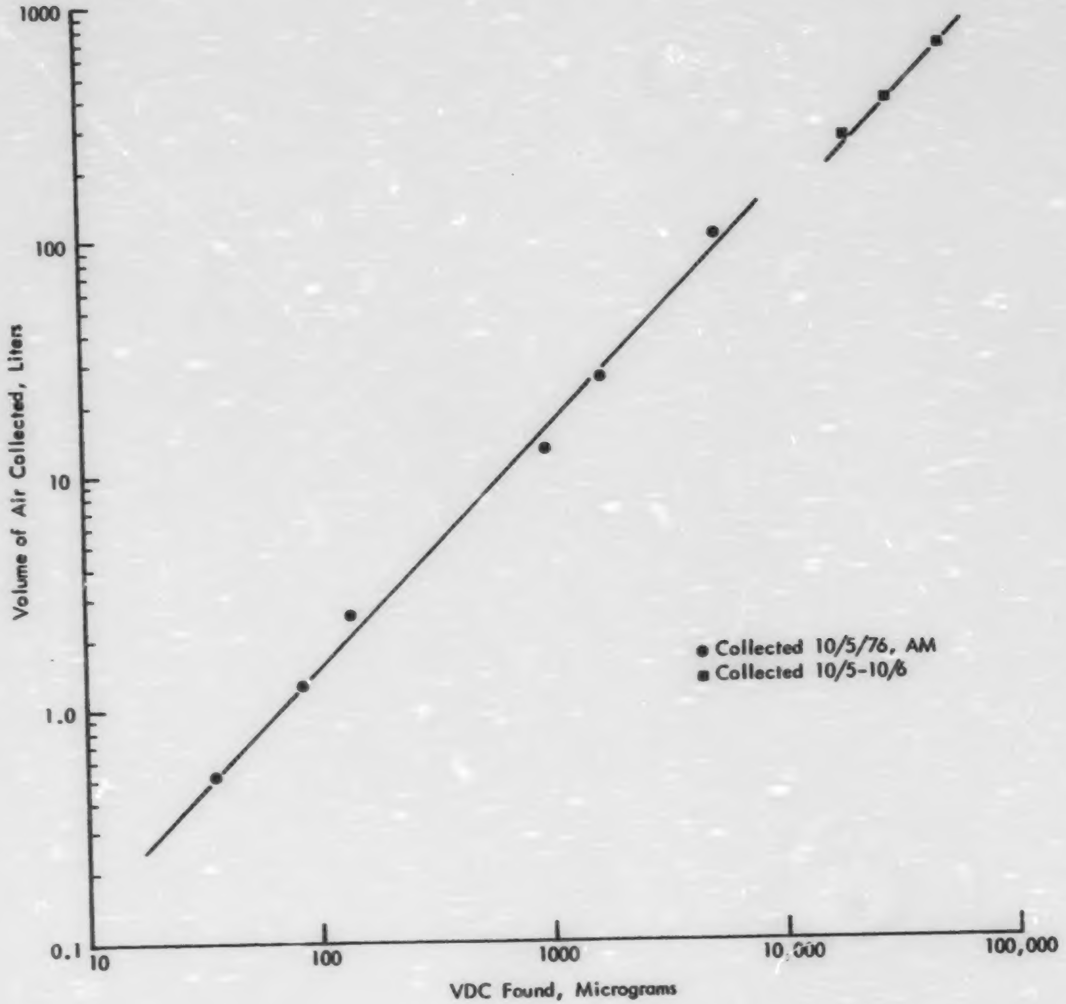

Figure 7.. Recovery of vinylidene chloride versus volume of air sampled

Table 11. STABILITY OF VDC ADSORBED ON CHARCOAL

Days after loading	VDC found (μg)[a]
2	187
5	192
8	195
12	180
16	195

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[a] Average of two analyses.

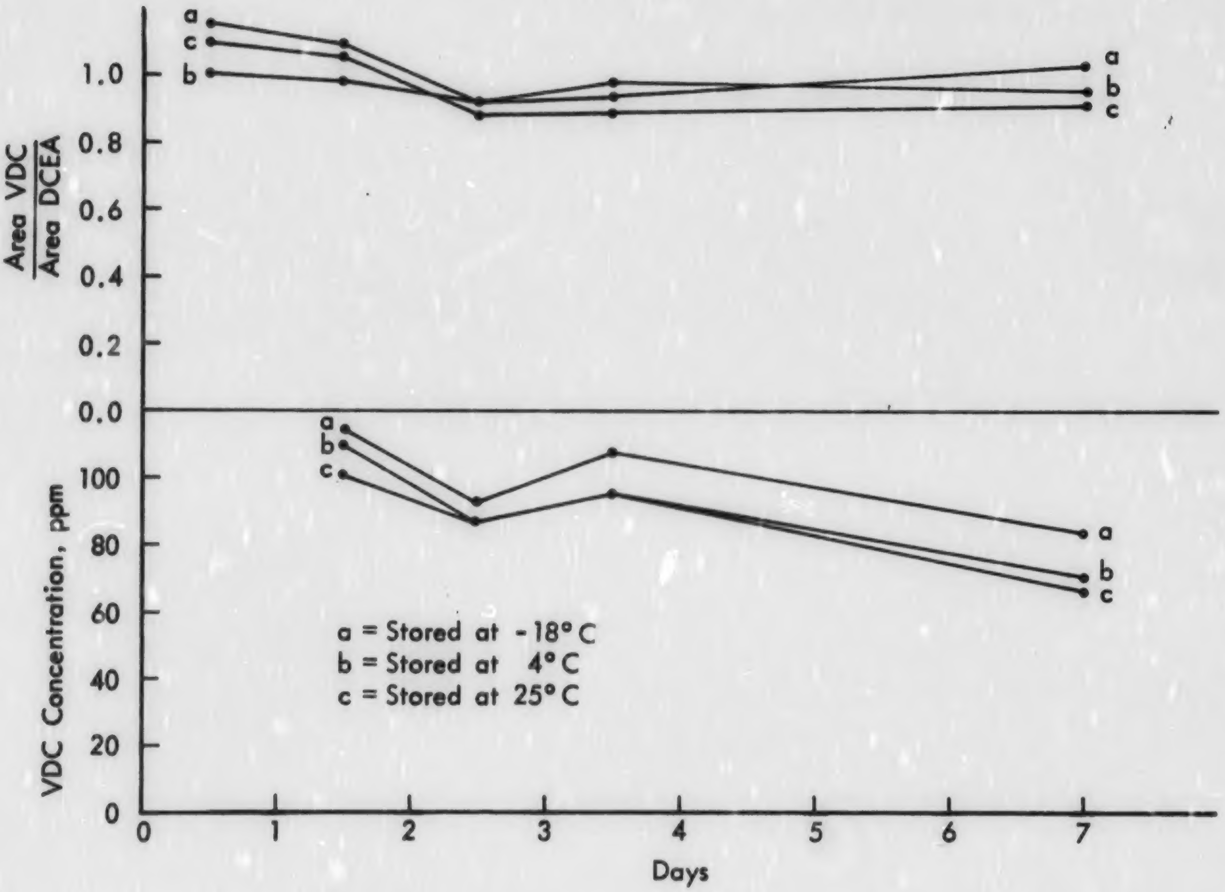

Figure 8. Stability of vinylidene chloride in carbon disulfide

Although some scatter was observed, two trends were observed. The ratio of peaks was relatively constant at all temperatures while the actual level of VDC decreased about 20% in the 7 days. This suggests that both VDC and DCEA were being lost at about the same rate, presumably by volatilization. As a result, standards are prepared fresh daily and samples were analyzed within 4 days.

Bromination of VDC - The presence of VDC in air samples must be confirmed and attempts to find a second GC column for confirmation were not successful. An alternate approach based upon the bromination of VDC to form 1,2-dibromo-1,1-dichloroethane was developed.

A preliminary experiment established that excess Br_2 was easily removed from the CS_2 by extraction with 0.5 M NaOH. A solution of 0.5 M Br_2 in CS_2 was completely debrominated by extracting twice with an equal volume of 0.5 M NaOH.

The two principal factors that were expected to affect the extent of bromination of VDC were (a) bromine concentration and (b) time. A solution of 100 ppm VDC in CS_2 was used to test these two variables. Initially, an increasing quantity of Br_2 was added to 2 ml of 100 ppm VDC in CS_2. Bromination was allowed to proceed 30 min after which the excess Br_2 was removed by extraction with 0.5 M NaOH. The CS_2 was then dried by passage through a microcolumn of Na_2SO_4 and analyzed for brominated VDC. The results shown in Figure 9 indicate that a 400-fold molar excess is required for maximum bromination. Subsequently an experiment to test the effect of bromination time was performed at a Br_2/VDC ratio of 470. The results shown in Figure 10 indicate that the bromination reaction was quite rapid and was judged to be essentially complete after 30 min. The optimum bromination conditions were considered to be a 400 molar excess of Br_2 and a reaction time of 30 min.

Water Samples

Purging Conditions - The volume of nitrogen required to completely purge the VDC from the water sample was determined using 5 ml of a 24-ppb solution. Quantitative sparging was achieved between 5 and 10 min using a gas flow of 38 ml/min. Sparging for 15 min at 38 ml/min resulted in a 30% loss of VDC. The optimum procedure was judged to be a purge time of 10 min at 38 ml/min.

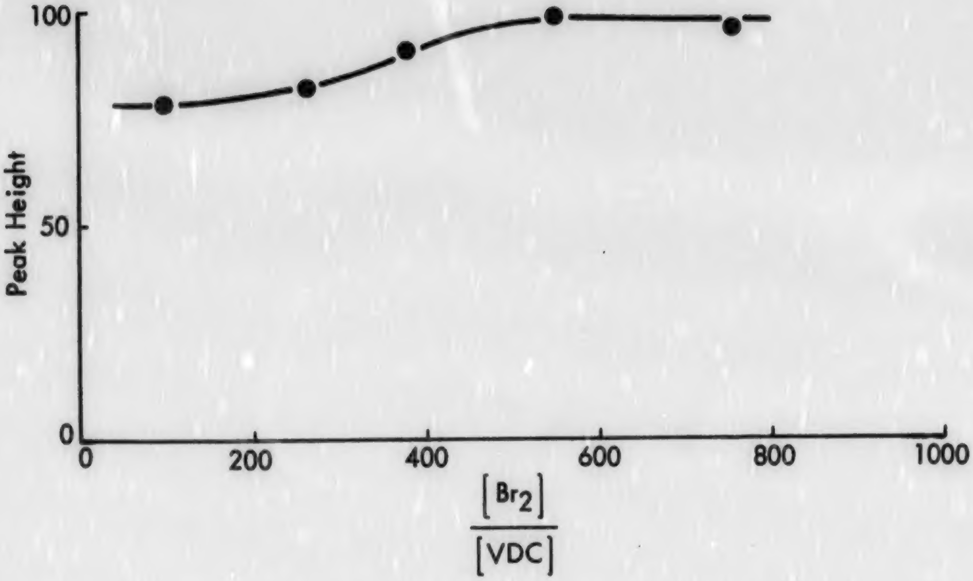

Figure 9. Bromination of vinylidene chloride: Effect of excess Br_2

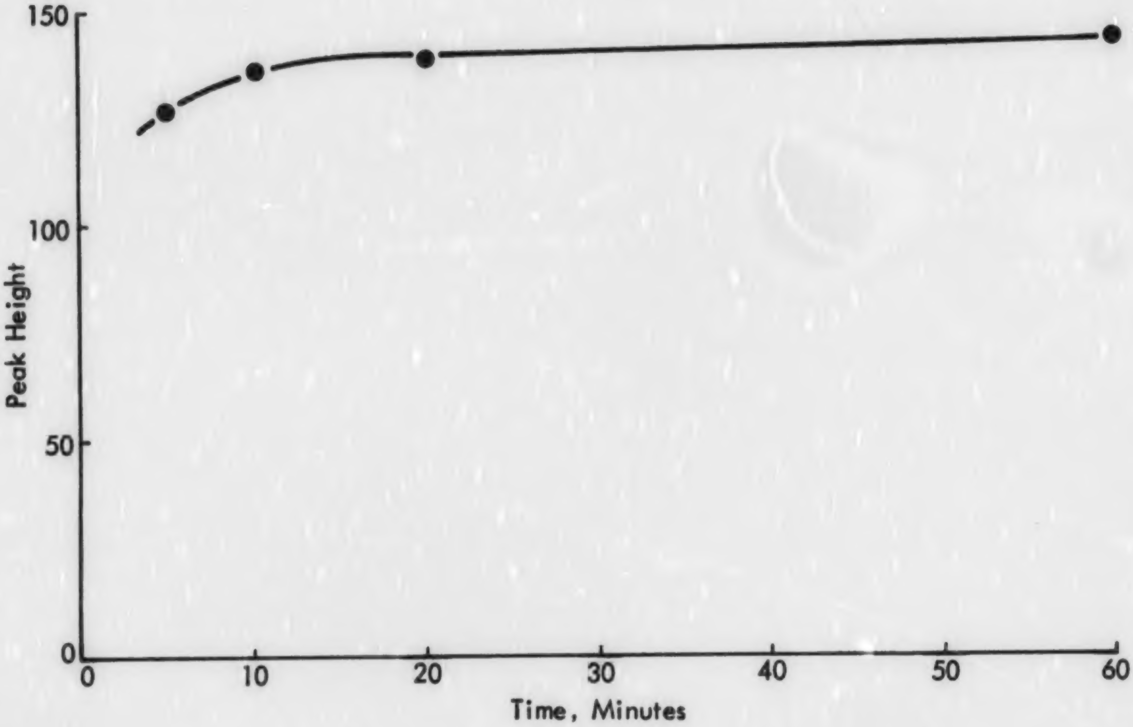

Figure 10. Bromination of vinylidene chloride: Effect of time

Standards and Calibration - A 12 ppt stock solution of VDC was made by injecting 1 ml of VDC (density = 1.218 g/ml) into 99 ml of 1-propanol. This solution was sotred in a refrigerator at 0°C. Working standards were prepared daily by injecting 25 µl of the stock standard into 100 ml of tap water resulting in a 3 ppm standard of VDC. In preparing VDC standards in water and in collecting samples, no headspace can be allowed to exist. After standard and sample preparation were carried out in the necessary volumetric flasks, clean glass vials were filled to overflowing with the respective solutions and sealed with caps containing Teflon®-rubber laminate septa (Pierce Chemical Company), so that ero headspace occurred.

Aliquots of from 10 to 100 µl of the 3 ppm solution in water were injected with 100 µl syringe into 5 ml of water in the VOA system and the VDC was purged as described previously. A calibration curve was generated on the Carbowax 1500 column and a plot of peak height (in mm versus ppb VDC) is shown in Figure 11. The detection limit was about 2 ppb and the curve was linear from 2 to 60 ppb.

Sample Storage and Stability - An 18-ppb standard of VDC in water was made by pipetting 1.5 ml of the 3 ppm standard in water into 250 ml of water in a volumetric flask. Five milliliters of the solution were analyzed immediately and the rest left to stand open in a hood. Samples were transferred to the VOA system by pouring the solution into the back of a 10 ml glass syringe to overflowing, then replacing the plunger and inserting it to the 5 ml level. This technique is used to insure that no headspace exists above the water during the transfer. A 5 ml aliquot of the open solution was analyzed on the VOA system after 25 min, 45 min, 2, 3, 4, and 5 hr. A calibration curve was prepared from the same stock solution.

The results showed a rapid loss of VDC from open aqueous solutions and confirm the requirement that water samples and standards must be stored with zero headspace.

Stability in another study of stability of VDC in water, a standard was prepared and poured to overflowing in five vials which were sealed with no headspace with Teflon®-rubber discs. One sample was analyzed immediately on the VOA system using the syringe technique described above and was found to be 12.5 VDC. The remaining four samples were stored in a refrigerator (at 4°C) and analyzed at intervals over a 9-day period.

The results of this study are listed in Table 12. It is apparent that VDC samples can be stored at 4°C for at least 9 days if no headspace is permitted.

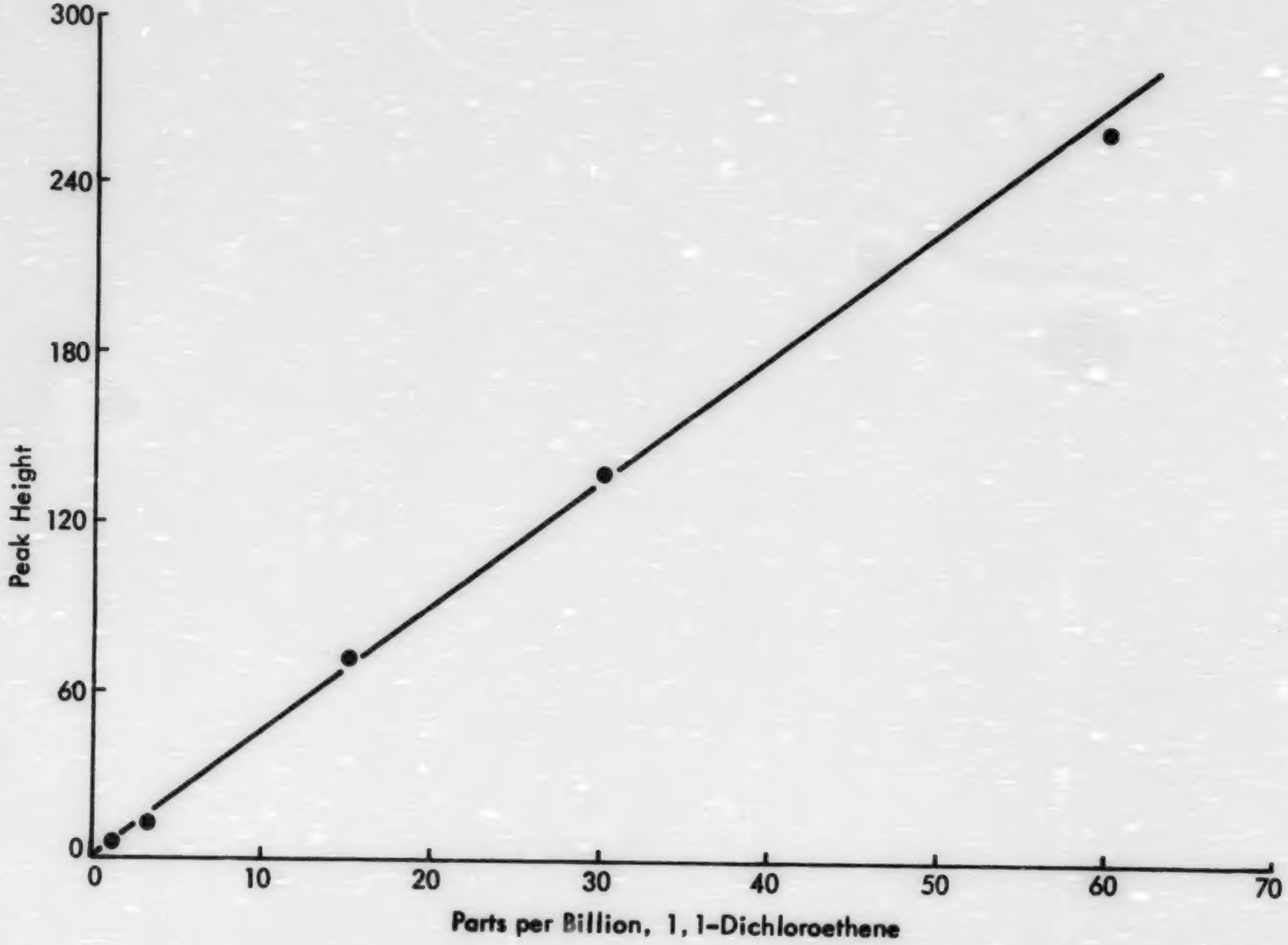

Figure 11. Calibration curve for vinylidene chloride by VOA technique

Table 12. STABILITY STUDY

Sample age (days)	Concentration (ppb)
0	13
3	15
6	11
9	16

Solid Samples

It was anticipated that a variety of commercial products manufactured from PVDC would be analyzed for residual monomer. The two general approaches are to either dissolve the product in an appropriate solvent or to thermally desorb the VDC from the product in a closed vessel and analyze the head space. Because of the wide variety of products with differing properties that will be tested, the second approach was judged to be the more promising.

A sample of PVDC/PVC powder was obtained from Aldrich Chemical Company, Milwaukee, Wisconsin, and used to evaluate the protocol. Samples of Saran Wrap, produced by Dow Chemical and purchased at a local grocery store, were also used in the evaluation. One- to 3-g quantities of the product were placed in a 14.6 ml crimp-seal vial which was then sealed. The vials were heated at 50, 75, 100, and 150°C for 15 to 90 min after which a 100-µl sample of head space gas was removed and analyzed. The gas chromatographic conditions were as follows.

Column: Glass 6 ft x 4 mm packed with 80/100 mesh Durapak OPN on Porasil C
Detector: Hydrogen flame ionization
Carrier: Nitrogen at 38 ml/min
Column Temperature: 90°C
Injector Temperature: 200°C
Detector Temperature: 275°C

The results obtained using the powder polymer are graphed in Figure 12. After approximately 30 min at 150°C, the polymer showed obvious signs of decomposition and VDC was no longer found in the head gas. At 50 and 75°C, very little VDC was released. Similarly, Saran Wrap showed extensive decomposition at 150°C and little VDC release at 50°C. The optimum conditions were judged to be a heating time of 90 min at a temperature of 100°C.

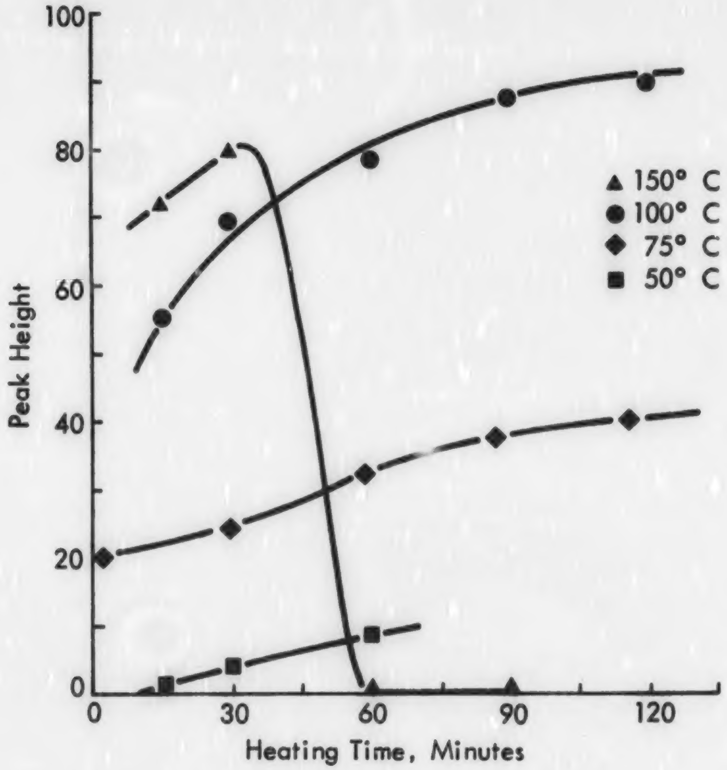

Figure 12. Release of vinylidene chloride from solids

This agrees well with the conditions employed by Dow Chemical of heating 60 min at 80°C.[2] Samples of a PVDC/PVC powder obtained from Aldrich Chemical Company, Milwaukee, Wisconsin, and Saran Wrap produced by Dow Chemical and purchased at a local grocery store were analyzed by this procedure. The results are summarized in Table 13.

Table 13. ANALYSIS OF SOLIDS

Sample	Sample weight	Sample volume	VDC (g/g)	
PVDC powder	1.00 g	0.7 cm 3	10.4	
PVDC powder	1.00 g	0.7 cm 3	9.3	
PVDC powder	1.00 g	0.7 cm 3	10.0	9.9 Average
Saran Wrap	1.86 g	1.4 cm 3	60	
Saran Wrap	2.00 g	1.5 cm 3	56	58 Average

The standard deviation and relative standard deviation for the PVDC powder analysis was 0.6 μg/g and 6%, respectively. The VDC level of the Saran Wrap was higher than expected. However, code numbers on the box indicate that the wrap was produced in 1974 when residual monomer levels were higher than present-day levels.

SECTION IV

SITE SELECTION

CRITERIA FOR THE SELECTION OF SAMPLING SITES

The objective of this task was to determine the exposure of the general public to 1,1-dichloroethene in populated areas adjacent to the most probable sources, from fabricated products, and from chlorinated drinking waters. The selected sampling locations were representative of the total industrial locations that are sources of VDC. The selected fabricated products and drinking waters were also representative of the total potential exposure by those media.

Criteria for the Selection of Industrial Sites

The selection criteria for choice of industrial locations were intended to achieve representative sampling, but at the same time, provide sites that were most likely to have detectable levels of VDC present. The criteria for the selection of industrial sites for sampling were:

- Estimated emission of VDC
- Polymerization technology
- Geographical location

Estimated Emissions of VDC - An estimate of the annual emissions of VDC from the various segments of the monomer synthesis, polymer synthesis and polymer processing industries has been reported. A summary of the estimated annual emissions is given in Table 14. According to this estimate, the majority of the emissions, 82.6%, are associated with monomer synthesis, while 16.7 and 0.7% occur with polymer synthesis and polymer fabrication, respectively.

Monomer is presently produced in the United States by Dow Chemical and PPG Industries at the plant locations listed in Table 15. Although PPG produces almost twice as much as Dow, approximately 155 million pounds

Table 14. MONOMER AND POLYMER SYNTHESIS AND POLYMER PROCESSING (1974)[a]/[3]

Process	Annual VDC emissions 1,000 kg	Annual VDC emissions 1,000 lb	VDC consumption (million lb)
Monomer synthesis	1,523[b]	3,355[b]	
Polymer synthesis	308	679	112
1. Latex for barrier coatings	55	120	20
2. Latex for miscellaneous coating	68[c]	150[c]	15
3. Synthetic fibers	73[c]	160[c]	16
4. Coating resin for cellophane	82	182[d]	25
5. Extrusion resin (emulsion process)	12	27[e]	21
6. Extrusion resin (suspension process)	18	40[f]	15
Fabrication or polymer processing	13.7	30.4	
1. Coating cellophane	0.7	1.6	
2. Coating plastics, paper and glassine	7.3	16.4	
3. Extrusion	0.2	0.4	
4. Miscellaneous coating	5.5[c]	12.0[c]	
Total	1,845	4,064	

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[a] This VDC emission inventory does not include emissions of VDC from the conversion of vinylidene chloride into 1,1,1-trichloroethane, because this conversion is not considered within the scope of this study.

[b] New emission-control technology will be installed in one of the plants during the latter part of 1975. On this basis, the annual VDC emissions should drop to 611,000 lb (277,000 kg).

[c] While all emissions listed in this table are estimates, the degree of certainty varies. These estimates are based on minimal data and are, therefore, more uncertain.

[d] These products result in vinyl chloride emissions. The annual emissions are 1,800 lb.

[e] These products result in vinyl chloride emissions. The annual emissions are 105,120 lb or 47,700 kg.

[f] These products result in vinyl chloride emissions. The annual emissions are 43,435 lb or 19,700 kg.

Table 15. PRODUCERS OF VINYLIDENE CHLORIDE MONOMER[3]

Manufacturer	Plant location	Production
PPG Industries	Lake Charles, Louisiana	170 to 175 x 10^6 lb
Dow Chemical	Freeport, Texas	90 to 95 x 10^6 lb
	Plaquemine, Louisiana	90 to 95 x 10^6 lb

or 89% is used captively for the synthesis of methyl chloroform. The remaining 20 to 25 million pounds plus 20 to 25 million pounds from Dow Chemical are sold to the merchant market. Dow retains approximately 70 million pounds for their own polymer synthesis. The estimate of emissions has been reported for the monomer industry, however, specific plants were not identified in the report. The average industry emission rate, based upon 1974 data, was 1.3 lb of VDC/100 lb of VDC manufactured. This may currently be less because one of the plants was scheduled to install improved emission control systems in late 1975. The emissions for the industry would then drop to 610,000 lb annually. Nevertheless, the plants producing monomer were given high priority in the selection of sampling sites.

The polymer synthesis industry can be conveniently divided into five groups based upon the end-use of the polymer produced. The emissions estimates have been based upon these five subcategories and are presented in Table 16. While the manufacturers within each subcategory were known, the emissions for the specific plants were not available. The largest companies within each area were known and as such were favored as potential sampling sites. Table 16 also lists the top one or two companies within each category. The synthetic fiber industry is unique in that they manufacture the VDC copolymer and then fabricate it into a filament. These filaments are marketed to the apparel and carpet industries where nonflammable fabrics are desired.

Emissions from the fabrication segment of the industry account for only a small fraction of the total and are distributed among a large number of fabricators. The estimated emissions from four types of fabricator industries are listed in Table 17.

The three companies that manufacture coated cellophane and the location of their plants are given in Table 18. The sizes of the companies are in the order listed. The emissions from cellophane plants appear to be fairly low.

Table 16. ESTIMATED ANNUAL EMISSIONS OF VDC IN POLYMER SYNTHESIS[3]

Polymer category	Leading plants	Total annual emissions for the industry (lb)	Emission of VDC (lb) per 100 lb of VDC polymerized
Barrier-coating latex	W. R. Grace, Owensboro, KY Morton Chemical Company Ringwood, IL	120,000	0.60
Miscellaneous coatings, latex	Dow Chemical, Midland, MI Standard Brands Chemical Industries Cheswold, DL Kensington, GA	150,000	1[a]
Synthetic fiber	Tennessee Eastman Kingsport, TN Monsanto, Decatur, AL	160,000	1[a]
Cellophane coating resin	Dow Chemical	182,000	0.7
Thermoplastic resins for extrusion	Dow Chemical	27,000 (emulsion) 40,000 (suspension)	0.13 0.26

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[a] Estimated.

Table 17. ESTIMATED ANNUAL EMISSIONS OF VDC IN POLYMER FABRICATION[3]

Fabrication area	Leading firm (total No. of companies)	Consumption of latex, dry bases (lb)	Annual VDC emissions (lb)
Glassine coating	Dixico Dallas, Texas (13 glassine and paper)	7,500,000	5,900
Paper coating	Crown Zellerbach Portland, Oregon (13 glassine and paper)	5,500,000	4,400
Paperboard coating	Unknown (6)	500,000	400
Plastic coating and miscellaneous	3M Decatur, Alabama (polyester) Allied Pittsburg, Pennsylvania (nylon) Hercules Covington, Virginia (polypropylene) Curwood New London, Wisconsin (polyethylene) (12)	7,000,000	2,160

Table 18. ESTIMATED ANNUAL EMISSIONS OF VDC IN CELLOPHANE COATING[3]/

Leading firms	Industry consumption of latex (dry basis, lb)	Estimated annual VDC emissions (lb)
Du Pont; Clinton, Iowa Tecumseh, Kansas		
FMC; Fredricksburg, Virginia Marcus Hook, Pennsylvania	26,000,000	1,560
Olin; Pisgah Forest, North Carolina Covington, Virginia		

Barrier-coating latex is used by the packaging industry to prepare heat-sealable coatings on paper and glassine, on paperboard and on plastic films. The final products are used largely to package food products. Of the over 30 companies reported to be barrier-coating latex users, two, Du Pont and Olin, are also manufacturers of the latex. The estimated annual emissions for the companies comprising the four types of coating substrates are given in Table 19 along with the company(s) that is a major factor in the market. A fabricator in the glassine or paper coating area is more likely to have a detectable level of VDC emissions.

Thermoplastic PVDC resin is primarily extruded into film products by the companies listed in Table 20. Amtech is the only company producing PVDC monofilament. Cryovac is the major consumer of extrusion resin produced by emulsion while Oscar Meyer is a larger consumer of suspension resin. No further breakdown of the emissions was reported. However, the industry as a whole appears to be a minor factor in the total emissions of the industry.

Polymerization Technology - A desirable site selection criterion was based upon the level of residual monomer remaining in the VDC copolymers. This level is influenced by whether a stripping or monomer reduction step was included in the polymerization process. Fabricators using polymers having a high residual monomer level would be expected to have higher VDC emissions. It appears, however, that monomer reduction is the industry practice and that it was impractical to apply this criterion.

Table 19. ESTIMATED EMISSIONS OF VDC IN THE PROCESSING OF PVDC POLYMERS[3]

Process	Annual VDC emissions kg	 lb	VDC emissions kg/100 kg (lb/100 lb) PVDC polymer
Coating cellophane	710	1,560	0.06
Coating plastics, paper	7,320	16,380	0.03
Glassine and paperboard extrusion	200	430	0.001
Miscellaneous coating	5,450	12,000	0.04
Total	13,680	30,370	

Table 20. MAJOR MANUFACTURERS OF EXTRUDED PVDC PRODUCTS[3]

Manufacturer	Plant location	Resin type
Cryovac (Division of W. R. Grace and Company)	Simpsonville, South Carolina Cedar Rapids, Iowa Camarilla, California Iowa Park, Texas	Emulsion and suspension
Oscar Meyer	Madison, Wisconsin Chicago, Illinois Davenport, Iowa Philadelphia, Pennsylvania Nashville, Tennessee Los Angeles, California	Emulsion and suspension
Dow Chemical	Midland, Michigan	Suspension
American Can Company	Cleveland, Ohio	Emulsion
Amtech, Inc.[a]	Odenton, Maryland	Suspension
Union Carbide Corporation	Centerville, Iowa	Suspension

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[a] Manufacture monofilament.

Geographical Distribution - The geographical location of the industrial plants selected for sampling was important so that the results from sample analysis can be used to establish whether exposure to VDC is a nationwide problem. The implementation of this criterion was restricted, however, by the following consideration: (a) efficiency of time and cost; and (b) the selection of sites most likely to have detectable levels of VDC.

Criteria for the Selection of Fabricated Products

Products were obtained for analysis that were representative of the five different types of polymerization industries.

Criteria for the Selection of Drinking Water Samples

Drinking water samples were requested from cities which were representatives of the major types of raw water sources in use in the United States. The selection was strongly influenced by whether: (a) VDC had been reported in the drinking water; and (b) the city was included in the National Organic Reconnaissance Survey (NORS). The first five cities selected for the NORS study of volatile organics were:

Miami, Florida
Seattle, Washington
Ottumwa, Iowa
Philadelphia, Pennsylvania
Cincinnati, Ohio

VDC had been found in the drinking waters of Cincinnati, Miami and Philadelphia but was not found at Ottumwa and Seattle. The second five cities to be surveyed were:

Tucson, Arizona
New York, New York
Grand Forks, North Dakota
Terrebonne Parish, Louisiana
Lawrence, Massachusetts

No results have been reported for these cities.

POTENTIAL SAMPLING SITES

Industrial Plants

With the criteria presented in the previous section as a guide, six industrial sites were selected and recommended for sampling. The plants are listed in Table 21 along with their location and other relevant production information.

Table 21. LOCATION AND PRODUCT PROFILE OF RECOMMENDED INDUSTRIAL SITES

Producer	Production site	EPA region	Type of facility	Products
Monomer				
Dow Chemical, USA	Plaquemine, Louisiana	VI	Producer of monomer	Chlorinated hydrocarbons, plastics and resins, glycols
PPG Industries	Lake Charles, Louisiana	VI	Producer of monomer; user of VDC to produce methyl chloroform	Chlorinated hydrocarbons including chloroethane
Polymer				
Dewey and Almy (Grace)	Owensboro, Kentucky	IV	Major producer of barrier-coating latex	PVC/PVDC resins, polyvinyl acetate resins, styrene-butadiene resins, polybutadiene-styrene latex
Dow Chemical, USA	Midland, Michigan	V	Only producer of thermoplastic and solvent-soluble polymers. Major producer of miscellaneous use polymers. Fabricater of extrusion resins.	Chlorinated hydrocarbons, brominated hydrocarbons, medicinals, pesticides, plasticizers, plastics and resins, general organic chemicals
Tennessee Eastman	Kingsport, Tennessee	IV	Producer of modacrylic fibers	General organic chemicals, plasticizers, plastics and resins, synthetic fibers (acrylic, modacrylic, polyester, cellulosic)
Fabricators				
Dixico	Dallas, Texas	VI	Major user of barrier-coating latex	Coated glassine

Two monomer production plants, PPG at Lake Charles, Louisiana, and Dow at Plaquemine, Louisiana, were selected, based largely on the fact that over 80% of the VDC emissions were believed to come from the monomer segment of the industry. Dow-Plaquemine was chosen rather than Dow-Freeport because it is in a more populated area and does not produce chloroethane.

The plants selected for sampling which synthesize polymers were Dewey and Almy (Division of Grace Chemical Company), Owensboro, Kentucky; Dow Chemical, Midland, Michigan; and Tennessee Eastman, Kingsport, Tennessee. Dewey and Almy was selected because it is the major producer of barrier-coating latex while Dow Chemical at Midland, Michigan, is the only producer of thermoplastic resin used for extrusion and solvent-soluble resin used for coating cellophane. Dow is also a major producer of resin for miscellaneous applications. The synthetic fiber industry is unique in that it is a polymer producer and a fabricator. The polymer is produced and then fabricated into a fiber at a single plant. Potential for emissions exists in the polymerization process as well as in the fabrication operations. Tennessee Eastman was chosen for sampling as the major producer of modacrylic fibers.

The plant selected to be representative of the fabrication segment of the industry could be a cellophane coater, user of barrier-coating latex or a user of thermoplastic resins. The emission data in Table 14 suggested that both the total emissions and the emissions per pound of PVDC polymer were small for cellophane coating and extrusion. The greatest emissions resulted from the use of barrier-coating latex. Of the two major users of barriercoating latex, Dixico, in Dallas, Texas, was in a more favorable geographical location for sampling during the winter months.

Fabricated Products

Fabricated products were requested from a wide spectrum of the fabricators.

Drinking Water Supplies

Drinking water samples were collected at pre- and post-chlorination points from the five cities listed in Table 22. Three were included in the first five-city NORS survey and two were in the second survey.

The geographical locations and EPA regions of the industrial plants and the water sample locations are shown in Figure 13.

Table 22. PROPERTIES AND PREVIOUS RESULTS OF FINISHED WATERS SELECTED FOR SAMPLING

City	Type of supply	Type of raw water	Inclusion in the NORS study	Results of NORS study
Cincinnati, Ohio	Surface	Industrial waste	Yes	a/
Lawrence, Massachusetts	b/	b/	Yes	c/
Miami, Florida	Ground	Natural waste	Yes	0.1 µg/liter VDC
New York, New York	b/	b/	Yes	c/
Philadelphia, Pennsylvania	Surface	Municipal waste	Yes	< 0.1 µg/liter VDC

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a/ VDC detected but not quantified.
b/ These data have not yet been obtained.
c/ No results have been announced.

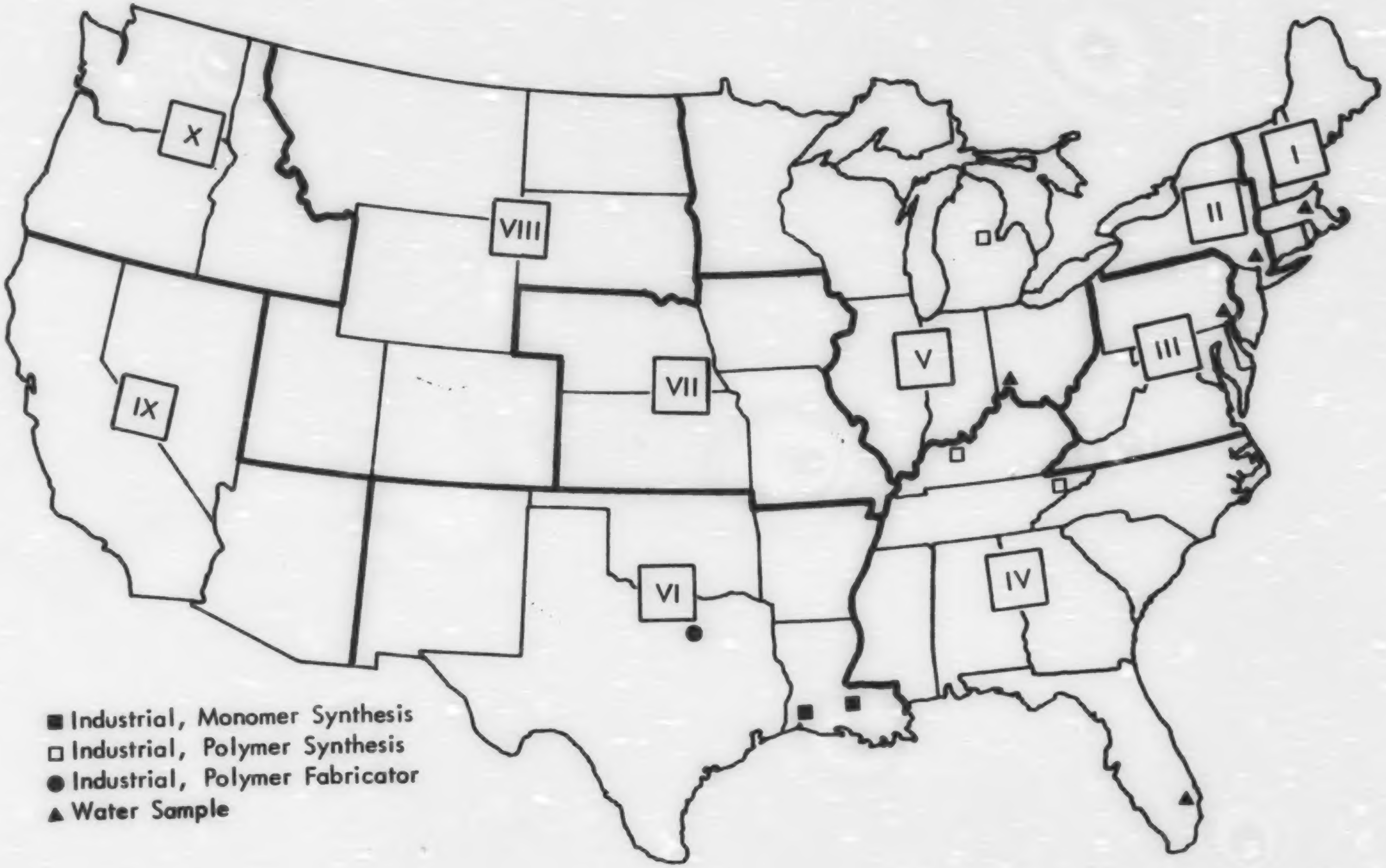
I
II
III
IV
V
VI
VII
VIII
IX
X
■ Industrial, Monomer Synthesis
□ Industrial, Polymer Synthesis
● Industrial, Polymer Fabricator
▲ Water Sample

Figure 13. Geographical Location of Recommended Sampling Sites

SECTION V

DISCUSSION OF RESULTS

The six selected industrial sites were sampled between January 4, 1977 and March 23, 1977. The actual sampling schedule is shown in Table 23; presampling site visits were conducted on the day prior to sampling. A summary of the air and water samples collected at the six industrial sites is given in Table 24 and a summary of the air sampling parameters follows in Table 25. The results from the six plants are discussed below followed by the results from analysis of drinking waters and solid products.

DOW CHEMICAL, PLAQUEMINE, LOUISIANA

Field Sampling

A presampling survey was conducted on January 3, 1977 immediately prior to the actual sampling. The plant lies mostly in Iberville Parish and is located in a rural area on the west bank of the Mississippi River. It has levees to the north, east, and southeast. A small Goodyear Tire and Rubber Company plant which produces polyvinylchloride resins is located immediately southeast of the plant. About 1-1/2 miles to the north-northwest is a plant owned by Copolymer Rubber and Chemical Corporation, producing ethylene-propylene copolymers.

The Dow facility manufactures chlorinated hydrocarbons, plastics, resins, and glycols. Approximately 95 million pounds of VDC are produced annually by Dow at Plaquemine and at Freeport, Texas.

The plant uses water from the Mississippi River. The processed wastewater is returned to the river at a point approximately 1/4 mile downstream of the intake. The winds in this area generally blow from the southeast, south, and north during the month of January and from the southeast, east, and north on an annual basis.

Table 23. SAMPLING SCHEDULE

Date	Company	Location	Product or operation
1/4-1/5	Dow Chemical	Plaquemine, Louisiana	VDC monomer
1/25-1/26	PPG	Lake Charles, Louisiana	VDC monomer
2/8-2/9	Dixico	Dallas, Texas	Fabricator
2/22-2/23	Dewey and Almy (Grace)	Owensboro, Kentucky	VDC polymer
3/8-3/9	Tennessee Eastman	Knoxville, Tennessee	VDC polymer and fabricator
3/22-3/23	Dow Chemical	Midland, Michigan	VDC polymer

Table 24. FIELD SAMPLING SUMMARY

Site	Air samples (stations x components)	Total samples (number/type)
Dow-Louisiana	13 x 2	26 Air 2 Water
PPG	12 x 2	28 Air 2 Water
Dixico	7 x 2	14 Air
Dewey and Almy	10 x 2	20 Air 2 Water
Tennessee Eastman	9 x 2	18 Air 4 Water
Dow-Michigan	13 x 2	26 Air 4 Water

Table 25. SUMMARY OF AIR SAMPLING PARAMETERS

Site	Average sampling volume (ℓ) (no. of samples)	Average sampling time (hr)	Rate (ℓ/min)
Dow-Louisiana	1,370 (13)	24.0	0.95
PPG	1,280 (12)	23.6	0.90
Dixico	1,330 (7)	23.5	0.94
Dewey and Almy	842 (10)	18.2	0.77
Tennessee Eastman	1,330 (9)	25.2	0.88
Dow-Michigan	1,155 (13)	23.2	0.83

Field sampling was carried out during the 24-hr period from 0800 January 4, 1977 until 0800 January 5, 1977. Thirteen air samplers were located at 12 sites upwind, downwind, and lateral with respect to the plant. Soil samples were taken north and south of the plant. Water samples were taken upstream and downstream from the point of discharge.

Air Sampling - Air sampling was conducted using 13 samplers at 12 sites. Two charcoal tubes were used in series for each sampling train. The sites were established upwind, laterally, and downwind of the plant with the majority initially being located downwind. Samplers were positioned at a height of 5 ft from ground level on public land such as right-of-ways and levees. Sampling sites were located at approximately 0, 1/4, 1/2, and 2/3 miles from the plant perimeter. Locations of the 12 sites are shown in Figure 14. Site descriptions and air sampling data are given in Table 26.

Water Sampling - Two grab water samples were obtained January 4, 1977. The upstream sample was taken from the Mississippi River at a point 0.9 miles upstream from the point of discharge. The downstream sample was taken 6 ft from the river bank, approximately 100 ft downstream from the point of discharge. The locations are indicated in Figure 14.

Meteorological Conditions - A summary of the weather conditions existing during the air sampling period is given in Table 27.

Analysis of Air Samples

VDC Levels - The results of the analysis of the 13 top charcoal tubes are listed in Table 28. VDC was detected in only seven of the samples, and then only at low levels. The amount of VDC found was close to the analytical limit of detection and made the analysis fairly difficult. For quality control, several unused charcoal tubes which had been shipped to the site were also analyzed and showed no evidence of VDC. The general absence of VDC raised concerns about the stability of the samples. For this reason, an aliquot of Sample No. 2 was spiked at 5 ppm (wt/v) VDC and analyzed repeatedly for 3 days. The VDC peak height on the chromatograms remained constant. The results demonstrated that any VDC in a CS_2 extract would be stable for at least 3 days, and that the absence of VDC in the sample extracts is not due to sample unstability.

The results of the analysis of the back-up tubes are also listed in Table 26. Evidence of VDC was found only in Samples Nos. 2 and 13, collected at North 0 miles, and West 0 miles, respectively. The amount of breakthrough was about 33% for Sample No. 2 and 20% for Sample No. 13. Sample 2 had the highest flow rate, 1.22 liters per minute for any site at which VDC was detected.

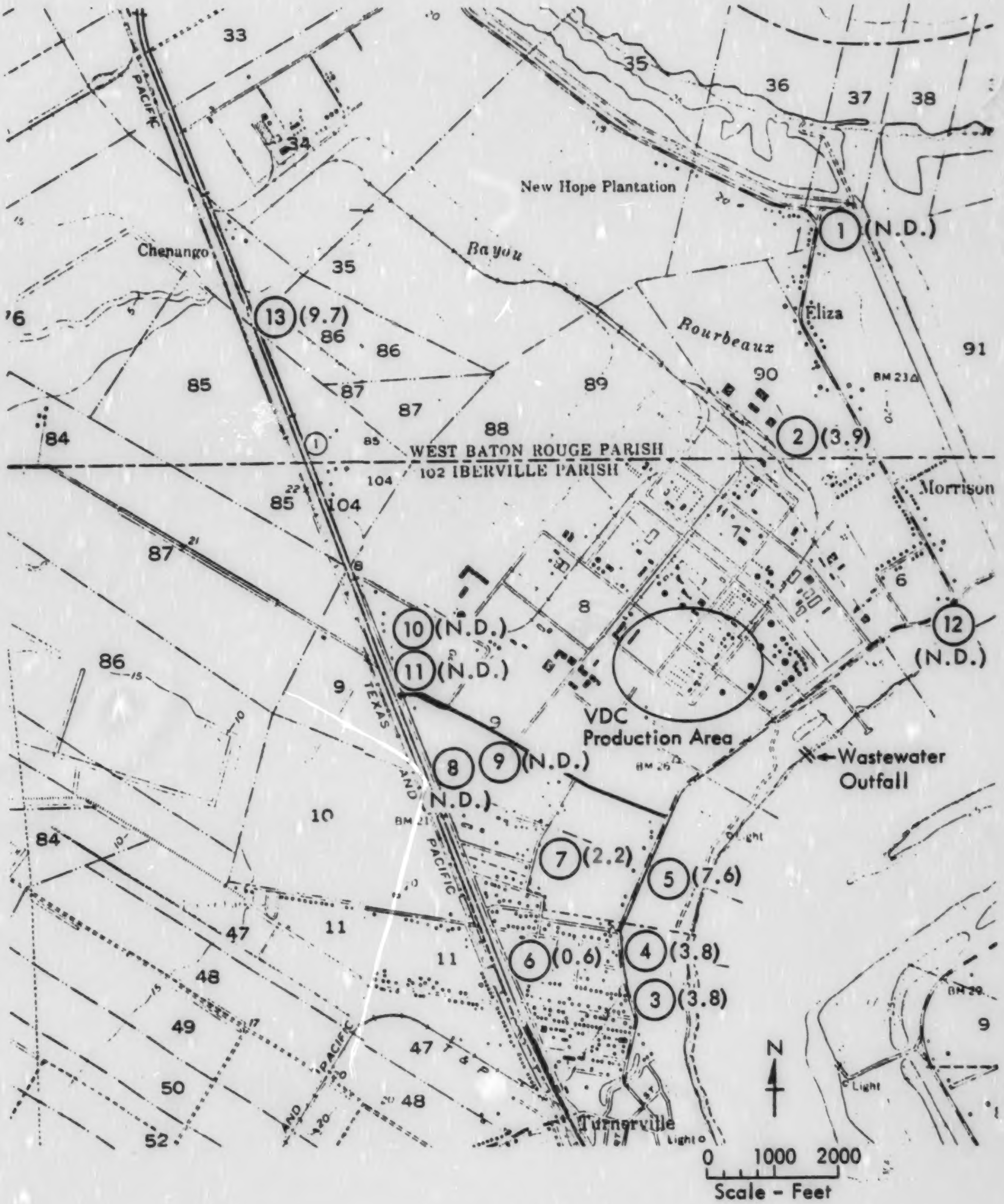
New Hope Plantation
1 (N.D.)
Chenango
Bayou
Bourbeaux
Eliza
13 (9.7)
2 (3.9)
WEST BATON ROUGE PARISH
102 IBERVILLE PARISH
Morrison
PACIFIC
TEXAS AND PACIFIC
10 (N.D.)
11 (N.D.)
12 (N.D.)
VDC Production Area
8 9 (N.D.)
N.D.)
Wastewater Outfall
7 (2.2)
5 (7.6)
4 (3.8)
6 (0.6)
3 (3.8)
Turnerville
N
0 1000 2000
Scale - Feet

Figure 14. Sampling Locations and Concentrations of VDC in Air at Dow Chemical, Plaquemine, Louisiana

Table 26. AIR SAMPLING DATA FOR DOW CHEMICAL, U.S.A., PLAQUEMINE, LA.

Area	Sample no.	Exact location	Totaling sampling (hr)	Sampling rate (ℓ/min)	Total volume (M^3)	Sample height (ft)
North transect, 1/2 mile	1	On La. 988, 0.3 miles north of Eliza	24.6	1.00	1.471	5.0
North transect. 0 mile	2	100 ft east of gate 3	24.6	1.22	1.794	5.0
South transect, 2/3 mile	3	New Erwin St. and Warren St.	23.8	1.09	1.561	5.0
South transect, 1/2 mile	4	Homestead St. and Warren St.	23.8	1.10	1.567	5.0
South transect, 1/4 mile	5	0.2 miles south La. 988 and La. 1148 on Warren St.	23.8	0.47	0.663	5.0
South Southwest transect, 2/3 mile	6	East Frontage Road for La. 1 at McDaniel St.	24.0	1.06	1.525	5.0
South Southwest transect, 1/4 mile	7	0.2 miles south of La. 1148 on Brownie St.	23.5	0.58	0.900	5.0
Southwest transect, 1/4 mile	8	East Frontage Road for La. 1, 0.2 miles south of La. 1148	24.1	0.95	1.376	5.0
Southwest transect, 0 mile	9	0.2 miles west of Brownie St. on La. 1148	23.5	0.67	0.946	5.0
West Southwest transect, 0 mile (1)	10	La. 1148 and the east Frontage Road of La. 1	23.6	1.39	1.961	5.0
West Southwest transect, 0 mile (2)	11	La. 1148 and the east Frontage Road of La. 1	23.6	0.64	0.843	5.0
East transect, 0 mile	12	East of La. 988, 1 mile north of La. 1148	24.2	1.39	2.012	5.0
West transect, 0 mile	13	0.4 miles north of La. 1148 on the east Frontage Road for La. 1	24.6	0.89	1.237	5.0

Table 27. WEATHER CONDITIONS DURING SAMPLING AT DOW CHEMICAL, USA, PLAQUEMINE, LA

Time	Wind Speed (Kts)	Wind Direction	Precipitation
January 4			
0700	5	SE	None
0800	6	E	None
0900	7	ESE	None
1000	10	SSE	None
1100	4	ESE	None
1200	5	SW	None
1300	4	NW	None
1400	5	ESE	None
1500	10	SE	None
1600	9	SE	None
1700	9	S	None
1800	7	SSE	None
1900	6	SSE	None
2000	5	SE	None
2100	00		None
2200	6	SSW	None
2300	5	S	Very light rain[a]
2400	6	SSE	Very light rain
January 5			
0100	00		Very light rain
0200	5	NNE	Very light rain
0300	00		Very light rain
0400	3	NE	Very light rain
0500	4	NNE	Very light rain
0600	00		Very light rain
0700	6	N	Very light rain
0800	8	N	Very light rain
0900	10	NNW	Very light rain

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[a] Reported as trace by the National Weather Service.

It is possible that some VDC would also breakthrough the second charcoal tube. Assuming that the same proportionality holds, the amount of VDC lost, 1.2 and 0.6 μg at Sites 2 and 13, respectively, would be barely detectable and would result in less than a 16% reduction in the total VDC reported. The total quantity (μg) found at each site is considered to be the sum of the top and bottom tubes, neglecting any possible loss due to breakthrough.

All top samples were brominated and analyzed for 1,2-dibromo-1,1-dichloroethane. The results are used only qualitatively due to the unavailability of a pure standard. Table 28 shows the results arranged to indicate confirmation of VDC by both the disappearance of a chromatographic peak on the OPN column following bromination and the appearance of a new peak on the OV-101 column also following bromination.

As expected, all the samples believed to contain VDC were confirmed. Most of the samples and blanks which had been shown not to contain VDC also did not contain 1,2-dibromo-1,1-dichloroethane. However, Samples Nos. 10, 11, and 12 were positive after bromination although analysis on the primary column did not indicate the presence of VDC. These are considered as false positives and cannot be explained.

The levels of VDC found in the air, as $\mu g/m^3$ given in Table 28 are shown in Figure 14. Figure 15 shows a wind rose pattern depicting the wind behavior during the time when the samples were being collected. At the beginning of the sampling period the wind was directly from the north, thus many of the sites were established to the south of the plant. Midway through the sampling, the wind shifted and was blowing from the southeast. The levels found to the south decreased as expected with increasing distance. The lower concentration at the southwest and west-southwest sites correlated well with the wind patterns. The highest concentration of 9.6 $\mu g/m^3$ was found at Site No. 13, located on the property line, approximately 1-1/2 miles west-northwest of the VDC production area. This site was the predominately downwind site. The predominately upwind site, No. 12, had no detectable VDC.

An attempt was made to confirm the presence of VDC by GC/MS. Sample No. 13 was chosen for GC/MS analysis as it had the highest level of VDC. Mass fragments from m/e 45 to 200 were collected and the presence of VDC was tested by an extracted ion current plot [EICP] of ions 61, 96, 98, 63 as shown in Figure 16. The results were too inconclusive to be considered as a confirmation.

Identification of Other Compounds - The analysis of the air samples by GC-FID, had shown qualitatively the presence of six to eight additional compounds. One sample, No. 13, was analyzed by GC/MS in order to confirm the presence of VDC and, if possible, establish the identity of the other peaks.

Table 28. VDC IN AIR SAMPLES FROM DOW CHEMICAL, PLAQUEMINE, LOUISIANA

					Confirmation by bromination			
Sampling station	Sampling[a] time	Volume (m^3)	Type of sample	VDC (μg)[b]	Loss of VDC[b]	Appearance of brominated VDC[c]	Presence of chloroethane	VDC ($\mu g/m^3$)
1	0755-0828	1.47	Top charcoal	ND[d]	NA[e]	NA	-	ND
			Backup charcoal	ND	NA	NA	-	
2	0747-0824	1.79	Top charcoal	5	Yes	Yes	No	3.9
			Backup charcoal	2	Yes	Yes	No	
3	0835-0825	1.56	Top charcoal	6	Yes	Yes	No	3.8
			Backup charcoal	ND	NA	NA	-	
4	0840-0829	1.57	Top charcoal	6	Yes	Yes	No	3.8
			Backup charcoal	ND	NA	NA	-	
5	0855-0832	0.66	Top charcoal	5	Yes	Yes	No	7.6
			Backup charcoal	ND	NA	NA	-	
6	0820-0820	1.53	Top charcoal	1	Yes	Yes	No	0.6
			Backup charcoal	ND	NA	NA	-	
7	0910-0837	0.90	Top charcoal	2	Yes	Yes	No	2.2
			Backup charcoal	ND	NA	NA	-	
8	0809-0816	1.38	Top charcoal	ND	NA	NA	-	ND
			Backup charcoal	ND	NA	NA	-	
9	0838-0800	1.96	Top charcoal	ND	NA	NA	-	ND
			Backup charcoal	ND	NA	NA	-	
10	0823-0801	0.84	Top charcoal	ND	NA	Yes	-	ND
			Backup charcoal	ND	NA	NA	-	
11	0823-0801	0.84	Top charcoal	ND	NA	Yes	-	ND
			Backup charcoal	ND	NA	NA	-	
12	0805-0815	2.01	Top charcoal	ND	NA	Yes	-	ND
			Backup charcoal	ND	NA	NA	-	
13	0730-0808	1.24	Top charcoal	10	Yes	Yes	No	9.7
			Backup charcoal	2	Yes	f/	No	

a/ 1/4/77 to 1/5/77.
b/ Based on analysis on Durapak OPN column.
c/ Based on analysis on OV-101 column.
d/ ND = Not detected.
e/ NA = Not applicable.
f/ Sample lost by evaporation.

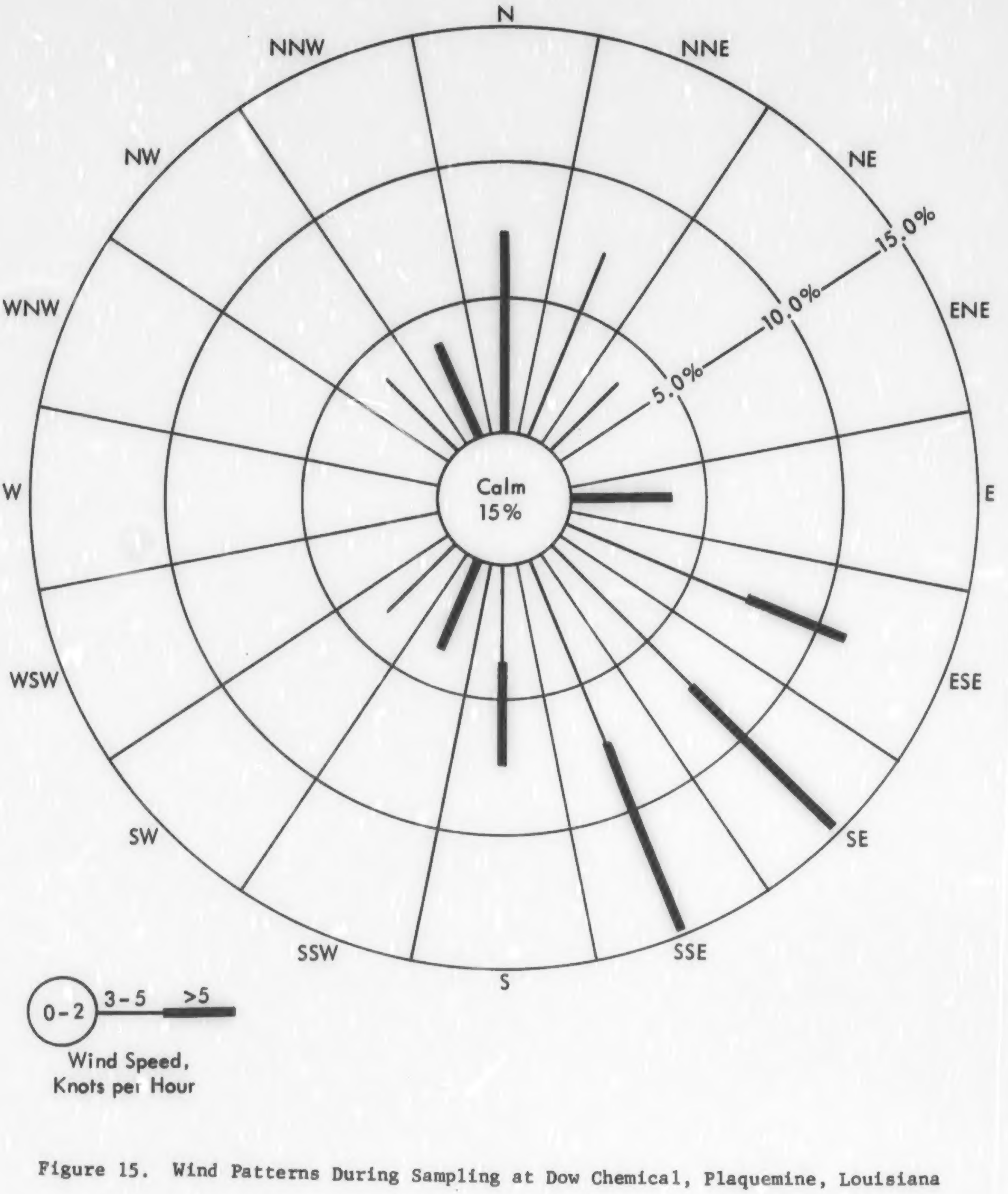

Figure 15. Wind Patterns During Sampling at Dow Chemical, Plaquemine, Louisiana

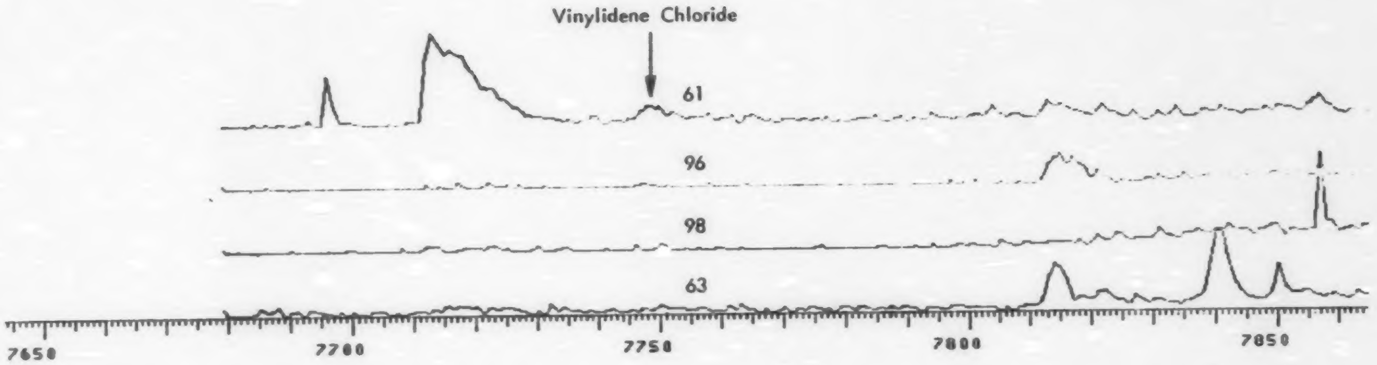

Figure 16. Extracted ion current plots - Dow air sample No. 13

The GC-FID analysis had shown two small peaks eluted before the solvent. An attempt was made to analyze these peaks on the GC/MS by not venting the solvent until it had appeared that they had entered the spectrometer. We were not able, however, to identify any of the peaks eluting before the solvent was vented. After 2 min the vent was closed for the remainder of the chromatographic run. This venting, however, did not completely prevent CS_2 from entering the spectrometer and contributing strongly to the total ion current. Because of the residual CS_2, it was not possible to obtain meaningful mass spectral data without using EICPs. From 3 to 4 m/e values, characteristic of the fragmentation of a specific compound, were plotted for the chromatographic run. The appearance of maxima for these ions coincidentally, at the retention time of a reference compound, or at the same spectrum number, in the correct intensity ratio, was considered as evidence for the presence of the compound. By this approach, seven compounds in addition to VDC were identified in Dow Chemical air Sample No. 13. The eight compounds are noted on the sum plot for Sample No. 13 given in Figure 17. Table 29 lists the compounds identified, the ions monitored with their expected and observed intensity ratios, and whether the compound is a company product. The confirmation of benzene was complicated by the presence of an intense 76 ion from CS_2 over the entire chromatogram.

The following compounds were shown by the EICP's to be absent; methyl chloride, ethyl chloride, trans-dichloroethylene, methylene chloride, cis-dichloroethylene, methyl chloroform, ethylene dichloride, 1,1,2-trichloroethane, and 1,2-dichloropropane.

Analysis of Water Samples

VDC Levels - The downstream and upstream water samples, W2 and W3, were first analyzed by flame ionization-gas chromatography. A sample size of 10 ml was used for the VOA procedure in conjunction with the Carbowax 1500 primary column. A small amount of VDC, approximately 2 ng, was found in the downstream sample, W2. In addition to the VDC, at least 18 other substances were detected. No VDC was detected in the upstream sample, W3, although at least four other components were present.

Both samples were then analyzed by GC/MS using identical gas chromatographic and analysis conditions. Examination of the mass spectra at the retention time of VDC failed to indicate the presence of VDC in either Sample W2 or W3.

An EICP current of the four largest fragment ions, 61, 96, 98, and 63, was obtained. It as not possible to discern the presence or absence of VDC in either sample due to the background noise.

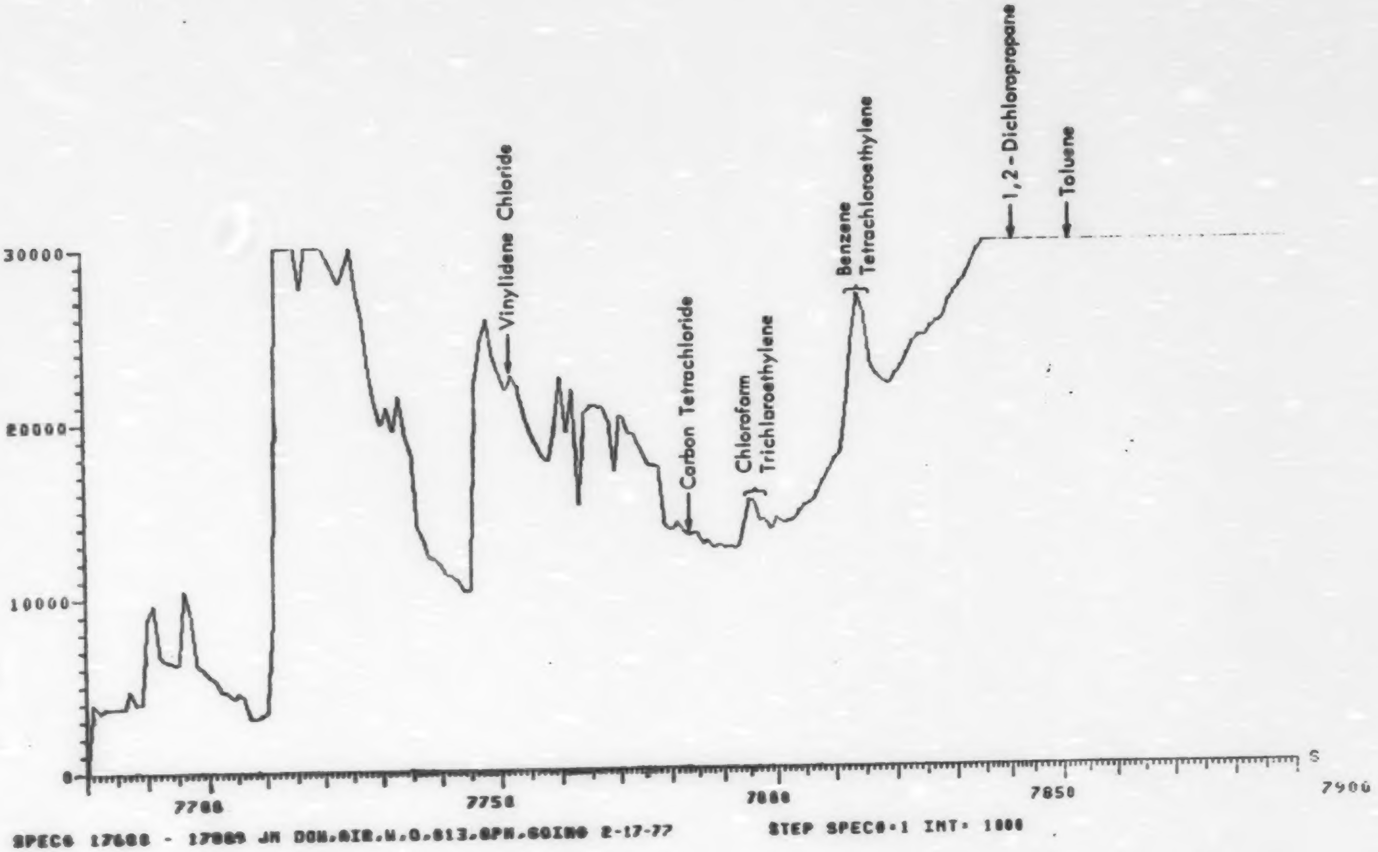

Figure 17. Sum plot of Dow air sample No. 13

Table 29. SUMMARY OF GC-MS ANALYSIS OF DOW AIR SAMPLE NO. 13

Compound	m/e values	Intensity ratios	Spectrum No.	Observed intensity ratios	Conclusion	Product
Vinylidene chloride	61, 96, 98, 63	1.00:0.53:0.36:0.28	17750	1.00:-:-:-	Present (?)	Yes
Carbon tetrachloride	119, 117, 121, 82	1.00:0.98:0.25:0.13	17783	1.00:0.7:0.3:-	Present	Yes
Chloroform	83, 85, 87, 47	1.00:0.55:0.07:0.14	17796	1.00:0.70:0.13:0.6	Present	No
Trichloroethylene	130, 132, 95, 97	1.00:0.95:0.85:0.59	17796	1.0:1.0:1.0:1.0	Present	No
Tetrachloroethylene	166, 164, 129, 131	1.00:0.78:0.75:0.65	17814	1.0:0.5:0.7:0.7	Present	Yes
Benzene	78, 76, 53, 79	1.00:0.06	17813	a/	Present (?)	No
Toluene	91, 92, 65	1.00:0.51:0.10	17851	1.00:0.50:0.35	Present	No
1,2-Dichloropropane	63, 62, 65, 76	1.00:0.44:0.30	17840	1.00:0.86:0.21	Present	Yes

---

a/ Ratio cannot be calculated as m/e 78 peak saturated.

The samples were then analyzed by GC/MS operated in the multiple ion scan (MIS) mode. Figure 18 shows the MIS plot obtained for 3 ng of VDC at m/e values of 61, 96, 93, 98, and 100. VDC eluted at 5.7 min (about 3.3 min in the Figure) with the five ions in an intensity ratio of 1.00: 0.47: 0.31: 0.24: 0.02, respectively. Figure 18 also shows the MIS plot of the same five ions for 10 ml of the downstream sample, W2. The relative intensity of the five ions monitored in Sample W2 was found to be 1.00: 0.47: 0.33: 0.24: and 0.03 which agrees well with the standard. This fact along with the matching retention times confirms the presence of VDC in the effluent. The relative intensity of the standard to the sample indicates that W2 contained about 4 ng VDC. The concentrations of VDC in the water from the GC/MS/MIS and the GC-FID analyses are given in Table 30 and agree quite well. The upstream sample was not analyzed by GC/MS/MIS.

Identification of Other Compounds - The GC-FID analysis for VDC had shown the presence of about 18 additional compounds in downstream water Sample W2. The sum plot from the GC/MS analysis showed about 13 distinct peaks. Initially EICPs were used to establish the identities of as many peaks as possible. The NPDES permit was used as a guide in selecting the compounds for screening.

Using this approach, 13 compounds in addition to VDC were identified. Table 31 lists the compounds which were established as being present along with the ions plotted plus their expected and actual intensity ratios. Also noted is whether the compound is listed as a plant product or is included in the plant's NPDES permit. The identified compounds are noted on the sum plot in Figure 19.

All but one peak in the sum plot were identified by EICPs plots. Its spectrum was obtained with background subtracted and searched against the Cyphernetics file using a Bieman search. The following matches and similarity indices were found:

Compound	Similarity index
Methylcyclohexane	0.397
Cycloheptane	0.318
3-Methyl-hexanol	0.307
1,1-Dimethylcyclopentane	0.305

The EICPs also established that the following compounds were not in the sample: vinyl chloride, methyl chloride, ethyl chloride, and 1,1-dichloroethane.

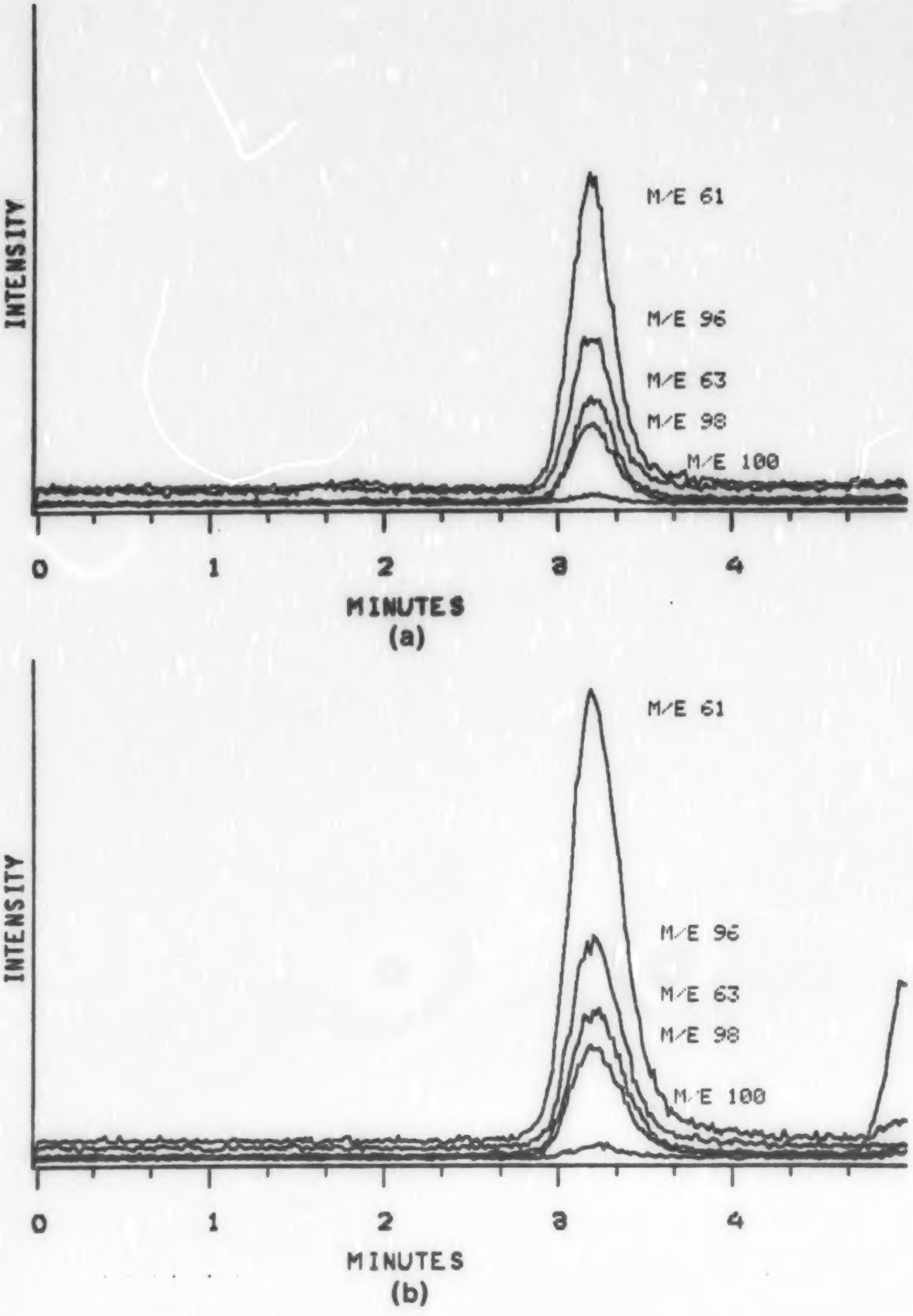

Figure 18. Multiple Ion Scan of 3 ng VDC and 10 ml of Dow Water Sample W-2

Scale Expanded x 10

a. 3 ng VDC
b. Dow Water Sample W-2

Table 30. VDC CONCENTRATIONS IN WATER FROM DOW CHEMICAL, PLAQUEMINE, LA.

Sample	Location	Volume	GC/FID	GC/MS	µg/L
W2	100 ft downstream of outfall	10 ml	2 ng	4 ng	0.2
W3	0.9 miles upstream of outfall	10 ml	N.D.	N.D.	N.D.

Table 31. SUMMARY OF GC-MS ANALYSIS OF DOW WATER SAMPLE W-2

Compound	m/e values	Intensity ratios	Spectrum No.	Observed intensity ratios	Conclusion	Product	NPDES permit
Methylene chloride	84, 86, 51, 88	1.00:0.60:0.33:0.10	6354	1.00:0.54:0.35:0.13	Present	Yes	Yes
Vinylidene chloride	61, 96, 98, 63	1.00:0.53:0.36:0.28	6371	a/	Present[a/]	Yes	Yes
trans-Dichloroethylene	61, 96, 98, 63	1.00:0.84:0.48:0.37	6390	1.00:0.67:0.67:-	Present (?)	No	No
cis-Dichloroethylene	61, 96, 98, 63	1.00:0.99:0.84:0.48	6396	1.00:0.57:-:-	Present (?)	No	No
Chloroform	83, 85, 87, 47	1.00:0.55:0.07:0.14	6401	1.00:0.56:0.28:0.09	Present	No	Yes
Ethylene dichloride	62, 64, 98, 100	1.00:0.31:0.08:0.06	6405	1.00:0.53:0.25:0.16	Present	Yes	Yes
Methyl chloroform	97, 99, 117, 119	1.00:0.62:0.19:0.19	6415	1.00:0.78:0.21:0.21	Present	No	No
Carbon tetrachloride	119, 117, 121, 82	1.00:0.98:0.25:0.13	6417	1.00:1.00:-:-	Present (?)	Yes	Yes
1,2-Dichloropropane	63, 63, 65, 76	1.00:0.44:0.30:0.11	6436	Peaks saturated	Present	Yes	Yes
Benzene	78, 77, 52	1.00:0.17:0.17	6438	Peaks saturated	Present	No	No
Trichloroethylene	130, 132, 95, 97	1.00:0.95:0.85:0.59	6440	1.00:1.20:1.20:1.00	Present (?)	No	No
1,1,2-Trichloroethane	83, 97, 85, 99	1.00:0.98:0.64:0.62	6451	1.00:0.88:0.50:0.63	Present	Yes	Yes
Tetrachloroethylene	166, 164, 129, 131	1.00:0.78:0.75:0.65	6499	1.00:0.83:0.77:0.77	Present	Yes	Yes
Toluene	91, 92, 65	1.00:0.51:0.10	6510	1.00:0.48:0.20	Present	No	No
Methyl cyclohexane	b/	b/	6462	-	Present	No	No

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a/ Presence of VDC confirmed by MIS.

b/ Determined by a Biemann search of the Cyphernetics file.

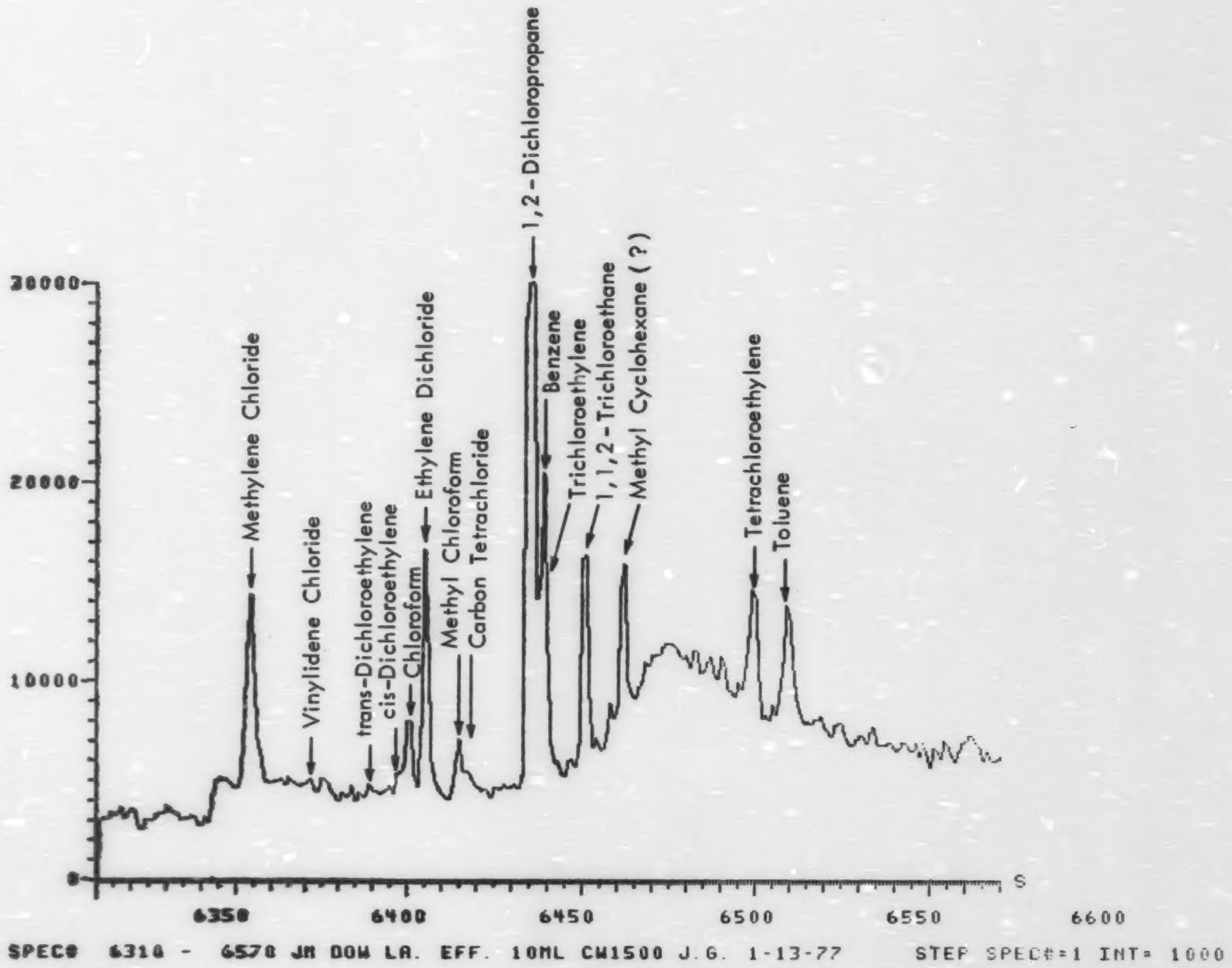


Figure 19. Sum plot of Dow water sample W-2

The upstream Sample W3 was also analyzed by GC/MS using identical procedures. The only peak which was observed on the sum plot was tentatively identified as hexane.

PPG INDUSTRIES, LAKE CHARLES, LOUISIANA

Field Sampling

A presampling survey was conducted on January 24, 1977 immediately prior to the actual sampling. The plant lies in Calcasieu Parish and is located just west of Lake Charles in the area bordered by I-10 and I-210. Olin Chemical has a plant located immediately to the northeast which produces ammonia, carbon monoxide, carbon dioxide, hydrazines, hydrogen, organic isocyanates, nitric acid, phosgene, polyether polyols, urea, sodium nitrite, and toluene 2,4-diamine. Certain-Teed Products has a plant located immediately to the northwest which produces polyvinylchloride resins.

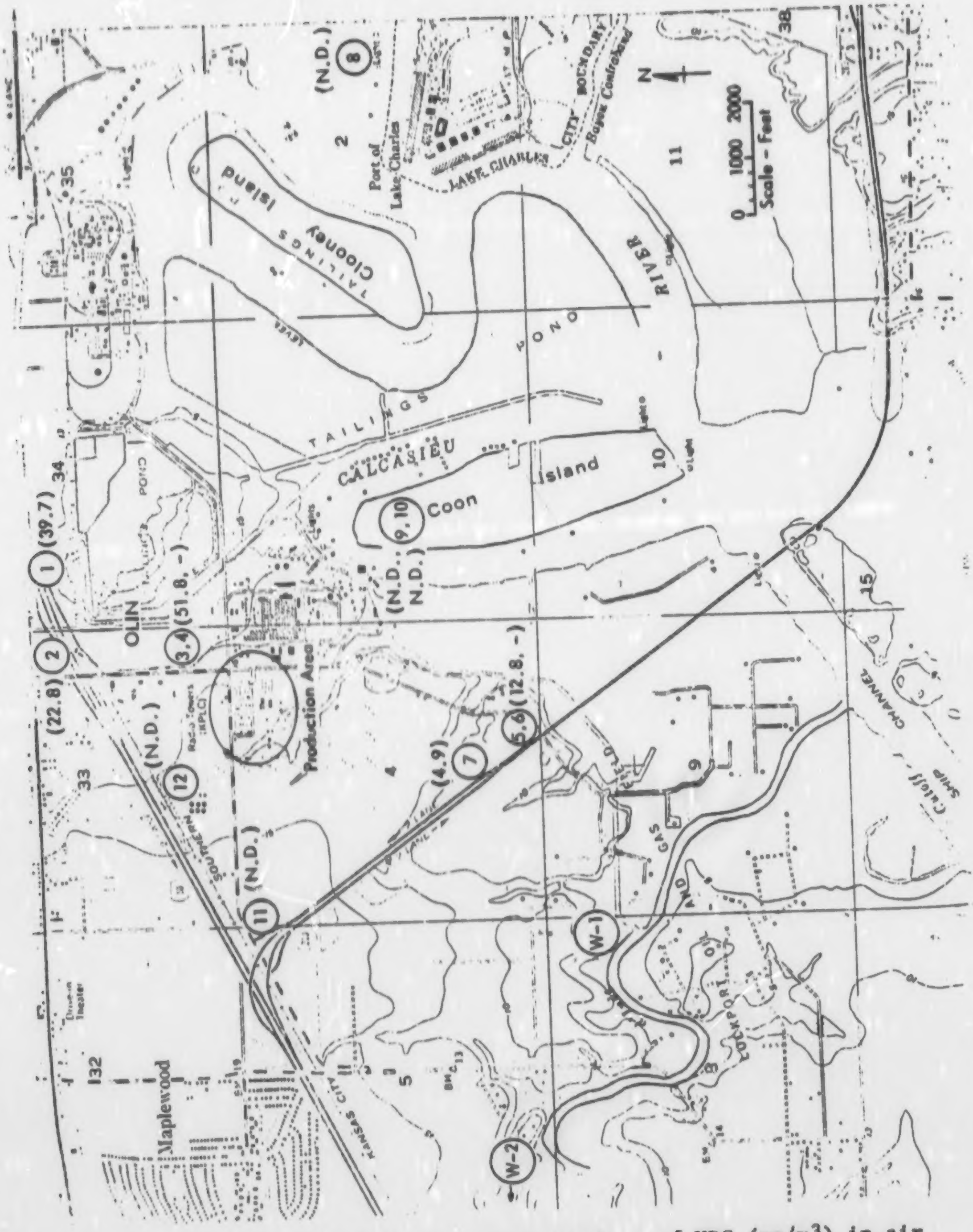
The PPG facility produces chlorine, ethyl chloride, ethylene dichloride, hydrochloric acid, hydrogen, perchloroethylene, sodium hydroxide, sodium silicates, 1,1,1-trichloroethane, vinyl chloride monomer, and vinylidene chloride monomer. Approximately 175 million pounds of VDC are produced annually by PPG in Lake Charles.

The plant uses water from the Calcasieu Ship Channel which is then discharged, by way of a canal, into the Bayou d' Inde. The wind blows predominantly from the north, southeast, south, and north-northwest during January and predominantly from the south, southeast, and north on an annual basis at Lake Charles.

Field sampling was carried out during the 29-hr period from 0700 January 25, 1977 until 1200 January 26, 1977.

Air Sampling - Air sampling was conducted using 12 samplers, each with two charcoal tubes in series, at nine different sites. The sites were established upwind, laterally, and downwind of the plant. Samplers were positioned at a height of 4 ft from ground level on public land such as right-of-ways. Samplers were located at approximately 0, 1/4, 1/2, 2/3, and 2 miles from the plant perimeter. Locations of the nine sites are shown in Figure 20. Site descriptions and air sampling data are given in Table 32. Duplicate samples were collected at the paired Sites 3 and 4, 6 and 6, and 9 and 10. At Sites 4 and 6, charcoal tubes were used which had been preloaded with approximately 285 µg VDC.

Water Sampling - Two grab water samples were obtained on January 25, 1977 and on January 27, 1977. The downstream sample was taken from the PPG canal at a point just before it enters the Bayou d' Inde. The upstream sample was taken from the west fork of Bayou d' Inde where it crosses under I-10. The locations are indicated in Figure 20.



1
(39.7)
2
(22.8)
3,4
(51.8, -)
5,6
(12.8, -)
7
(4.9)
8
(N.D.)
9,10
(N.D.
N.D.)
11
(N.D.)
12
(N.D.)
W-1
W-2
OLIN
Production Area
Radio Towers
SOUTHERN
KANSAS CITY
Maplewood
Drive-in Theater
TAILINGS POND
TAILINGS
Clooney Island
Coon Island
CALCASIEU RIVER
Port of Lake Charles
LAKE CHARLES
CITY BOUNDARY
Bayou Contraband
GAS AND OIL
LOCKPORT
Cutoff Ship Channel
CHANNEL
POND
LEVEE
N
0 1000 2000
Scale - Feet
132
33
34
35
2
11
38
15
10
9
4
5

Figure 20. Sampling locations and concentrations of VDC (µg/m3) in air at PPG Industries, Lake Charles, Louisiana

Table 32. AIR SAMPLING DATA FOR PPG INDUSTRIES, LAKE CHARLES, LA.

Area	Sample no.	Exact location	Total sampling (hr)	Sampling rate (/min)	Total volume (M^3)	Sample height (ft)
Northeast transect, 0.5 miles	1	US-90 and Columbia Southern Road	24.00	0.936	1.346	4.0
North transect, 0.5 miles	2	0.5 miles north of gate	23.78	0.887	1.266	4.0
North transect, 0 miles	3	150 ft north of gate	23.85	0.960	1.374	4.0
North transect, 0 miles	4	150 ft north of gate	23.82	1.012	1.447	4.0
South transect, 0 miles	5	West end of I-210 bridge	23.22	0.930	1.296	4.0
South transect, 0 miles	6	West end of I-210 bridge	23.20	0.983	1.368	4.0
Southwest transect, 0 miles	7	0.2 miles north of I-210 bridge	23.12	1.043	1.447	4.0
East transect, 2 miles	8	North end of old US-90 bridge	24.13	0.977	1.413	4.0
Southeast transect, 0.25 miles	9	Coon Island	23.92	0.920	1.320	4.0
Southeast transect, 0.25 miles	10	Coon Island	23.92	0.250	0.359	4.0
West transect, 0.5 miles	11	Junction of I-210 and Maplewood Road	23.03	0.965	1.333	4.0
Northwest transect, 0.67 miles	12	0.5 miles east of I-210 on Maplewood Road	23.50	0.932	1.314	4.0

Meteorological Conditions - A summary of the weather conditions existing during the air sampling period is given in Table 33.

Analysis of Air Samples

VDC Levels - The results of the analysis of the charcoal tubes are listed in Table 34. VDC was detected at 5 of the 10 sampling stations. VDC was present in all five top charcoal tubes and in four of five bottom charcoal tubes. As was the case with the Dow samples from Plaquemine, Louisiana, some breakthrough at the 1 liter/min sampling rate did occur, ranging from 24 to 48% of total VDC found. The higher percentage of breakthrough was associated with the higher total quantities of VDC trapped. The effect of the breakthrough is to slightly bias the results to the low side. If a lower flow rate had been used to reduce the breakthrough, then the total VDC collected would have been less, thus lowering the quality of all the data.

All nine samples believed to contain VDC were confirmed by bromination. Table 34 indicates the results both in terms of whether the VDC peak was eliminated by bromination and whether a peak appeared for brominated VDC. In all cases, VDC was confirmed. Moreover, the bromination confirmed that no chloroethane had been collected and therefore was not co-eluting with VDC. Thus, no correction had to be applied to the results to account for chloroethane.

At Sites 4 and 6, duplicate air samplers were operated concurrently using charcoal tubes that had been spiked at Midwest Research Institute (MRI) with VDC. The tubes were spiked from an inhalation chamber that at the time contained numerous test animals. The tubes were expected to have been loaded with ~ 300 μg VDC; however, this is only approximate in that we had no knowledge of the homogeniety of the chamber. (A third tube was stored at MRI as a control.) The purpose of the experiment was to show that nothing in the air collected around an industrial chemical plant, e.g., Cl_2, NO_x, or PAN's, would cause a decomposition of the trapped VDC. Upon analysis, 290, 672, and 605 μg of VDC were found for samples from Site 4, Site 6, and MRI, respectively.

The objective of the experiment, to demonstrate that VDC trapped by the charcoal was not being decomposed by some common atmospheric contaminant, was met. The discrepancies in the micrograms VDC found were probably due to uncontrollable variables in the spiking.

Table 33. WEATHER CONDITIONS DURING SAMPLING AT PPG INDUSTRIES, LAKE CHARLES, LA.

Time	Wind		Precipitation
	Speed (Kts)	Direction	
January 25			
0700	5	NW	None
0800	4	NW	None
0900	5	NNW	None
1000	4	NE	None
1100	7	N	None
1200	6	N	None
1300	7	N	None
1400	6	NNW	None
1500	5	W	None
1600	7	NW	None
1700	8	SSW	None
1800	9	SSW	None
1900	7	SW	None
2000	5	SW	None
2100	5	SW	None
2200	5	S	None
2300	0	N	None
2400	4	WSW	None
January 26			
0100	5	WSW	None
0200	3	SW	None
0300	4	S	None
0400	3	S	None
0500	3	SSW	None
0600	3	S	None
0700	3	S	None
0800	3	SSE	None
0900	4	SSE	None
1000	6	S	None
1100	8	S	None
1200	7	S	None

Table 34. VDC CONCENTRATIONS IN AIR SAMPLES FROM PPG INDUSTRIES, LAKE CHARLES, LOUISIANA

					Confirmation by bromination			
Sampling station	Sampling[a/] time	Volume (m^3)	Type of sample	VDC (µg)[b/]	Loss of VDC[b/]	Appearance of brominated VDC[c/]	Presence of chloroethane	VDC (µg/m^3)
1	0800-0800	1.36	Top charcoal	31	Yes	Yes	No	39.7
			Backup charcoal	23	Yes	Yes	No	
2	0820-0807	1.27	Top charcoal	22	Yes	Yes	No	22.8
			Backup charcoal	7	Yes	Yes	No	
3	0812-0803	1.37	Top charcoal	37	Yes	Yes	No	51.8
			Backup charcoal	34	Yes	Yes	No	
4	0813-0803	1.45	Top charcoal	290	Yes	Yes	No	-
			Backup charcoal	No sample	No sample	No sample	-	f/
5	0907-0820	1.30	Top charcoal	12.6	Yes	Yes	No	12.8
			Backup charcoal	4	Yes	Yes	No	
6	0908-0820	1.37	Top charcoal	672	Yes	Yes	No	f/
			Backup charcoal	No sample	No sample	No sample	-	
7	0917-0824	1.48	Top charcoal	7.2	Yes	Yes	No	4.9
			Backup charcoal	ND[d/]	NA[e/]	NA	-	
8	0745-0753	1.41	Top charcoal	ND	NA	ND	No	ND
			Backup charcoal	NA	NA	NA	-	
9	1120-1115	1.32	Top charcoal	ND	NA	ND	No	ND
			Backup charcoal	NA	NA	NA	-	
10	1120-1115	0.36	Top charcoal	ND	NA	ND	No	ND
			Backup charcoal	NA	NA	NA	-	
11	0925-0827	1.33	Top charcoal	ND	NA	ND	No	ND
			Backup charcoal	-	NA	NA	-	
12	0845-0815	1.31	Top charcoal	ND	NA	ND	No	ND
			Backup charcoal	-	NA	NA	-	
Field	-	-	Top charcoal	ND	NA	ND	No	ND
Blank			Backup charcoal	ND	NA	NA	-	
Field	-	-	Top charcoal	605	Yes	Yes	-	f/
Spike			Backup charcoal	No sample	No sample	No sample	-	

a/ 1/25/77-1/26/77.
b/ Based on analysis using Durapak OPN column.
c/ Based on analysis using OV-101 column.
d/ ND = not detected.
e/ NA = not applicable.
f/ Spiked sample.

The levels of VDC found in the air, as µg/m^3 were given in Table 34 and are shown in Figure 20. Figure 21 shows a wind rose pattern depicting the wind behavior at Lake Charles Municipal Airport during the time when samples were being collected. The wind was from the north during the first one-third of the sampling period, and then blew from the south for the remaining time. The concentrations found correlate quite nicely with the wind patterns. The highest level, 51.8 µg/m^3, was found at the station on the north plant boundary at 0 mile. The sites farther north have lower concentrations that correlate with the wind direction. VDC, at 12.8 and 4.9 µg/m^3, was found at the two sites directly south of the plant. No VDC was found at any of the east or west sites which were never downwind of the plant.

The presence of VDC in two air samples, Nos. 3 and 5, was confirmed by GC/MS. Mass spectra were collected from m/e 45 to 200 and the presence of VDC was tested by EICPs from ions 61, 96, 98, and 63. As seen in Figure 22, VDC was confirmed in air Samples Nos. 3 and 5.

Identification of Other Compounds - The analysis of the air samples by GC-FID had indicated the presence of seven to nine compounds in addition to VDC. These compounds were particularly noticeable in the downwind samples such as Nos. 1, 2, 3, 5, and 7. The north and south fence line samples, Nos. 3 and 5, respectively, were analyzed by GC/MS to confirm VDC and provide identifications of the additional peaks. Specific compounds were identified using EICPs. Tables 35 and 36 list the compounds found in air Samples Nos. 3 and 5, respectively, as well as the ions monitored, their expected and observed intensities and whether the compound is a company product. The compounds found at the two sites were the same except for the probable presence of *cis*- and *trans*-dichloroethylene and the presence of toluene and 1,1,2-trichloroethane at the No. 5 site, south boundary. Sum plots for air Samples Nos. 3 and 5 are given in Figures 23 and 24, respectively, showing the compounds identified.

The following compounds were shown by EICPs not be present; methyl chloride, vinyl chloride, ethyl chloride, *trans*-dichloroethylene, methyl chloroform, *cis*-dichloroethylene, ethylene dichloride, toluene, 1,1,2trichloroethane and 1,2-dichloropropane.

Analysis of Water Samples

VDC Levels - The downstream water sample, W1, and the upstream sample, W2, were first analyzed by GC-FID. Sample W1 was found to contain 550 ppb VDC while W2 contained no VDC. The results are given in Table 37. The sample was then analyzed by GC/MS using the same conditions applied to the Dow Chemical, Plaquemine, Louisiana, water sample. Figure 25 shows a sum plot for the analysis of 1 ml of the PPG effluent, with the VDC peak identified. The presence of VDC was confirmed by the comparison to a known spectrum as shown in Figure 26.

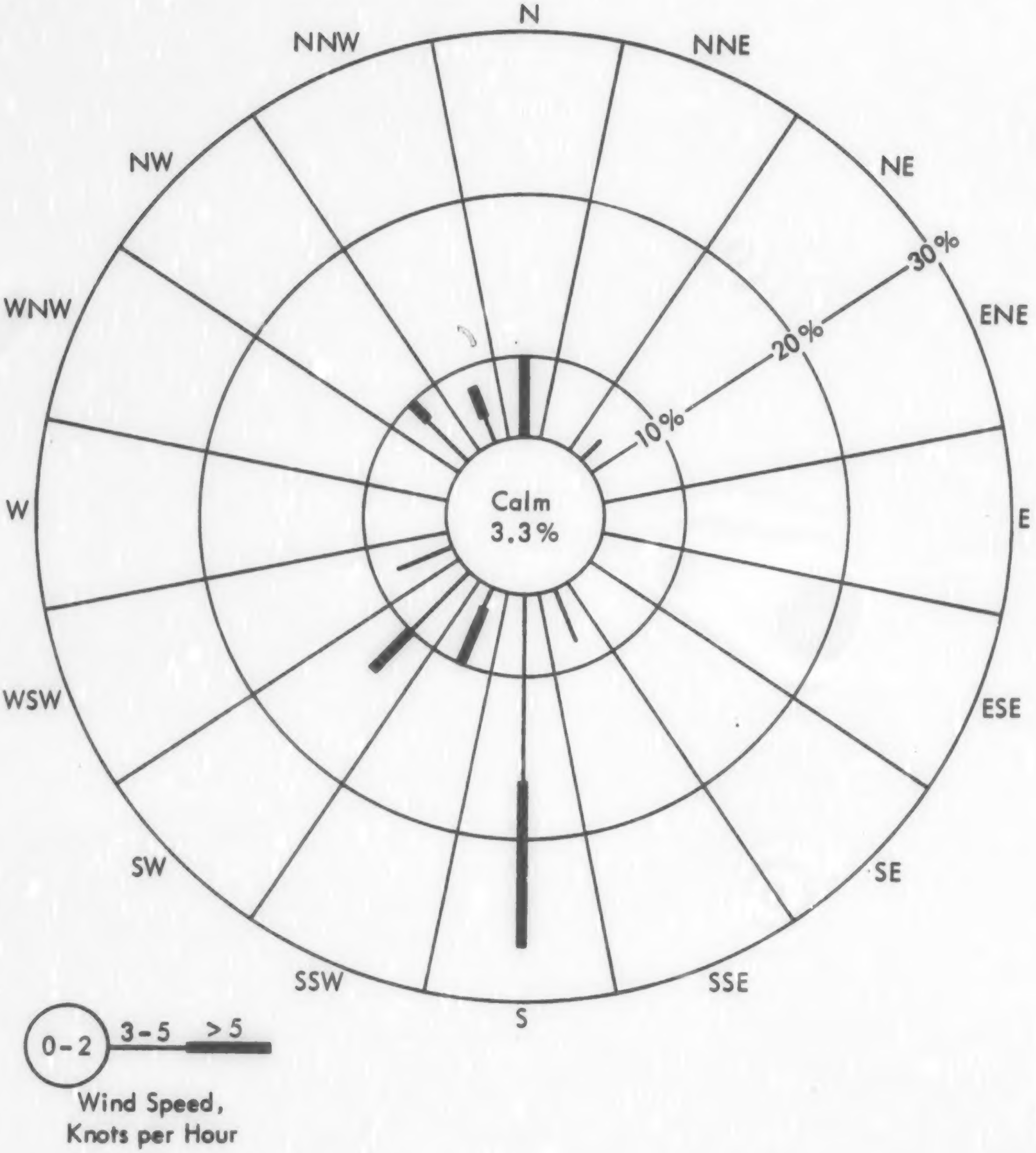


Figure 21. Wind patterns during sampling at PPG Industries, Lake Charles, Louisiana

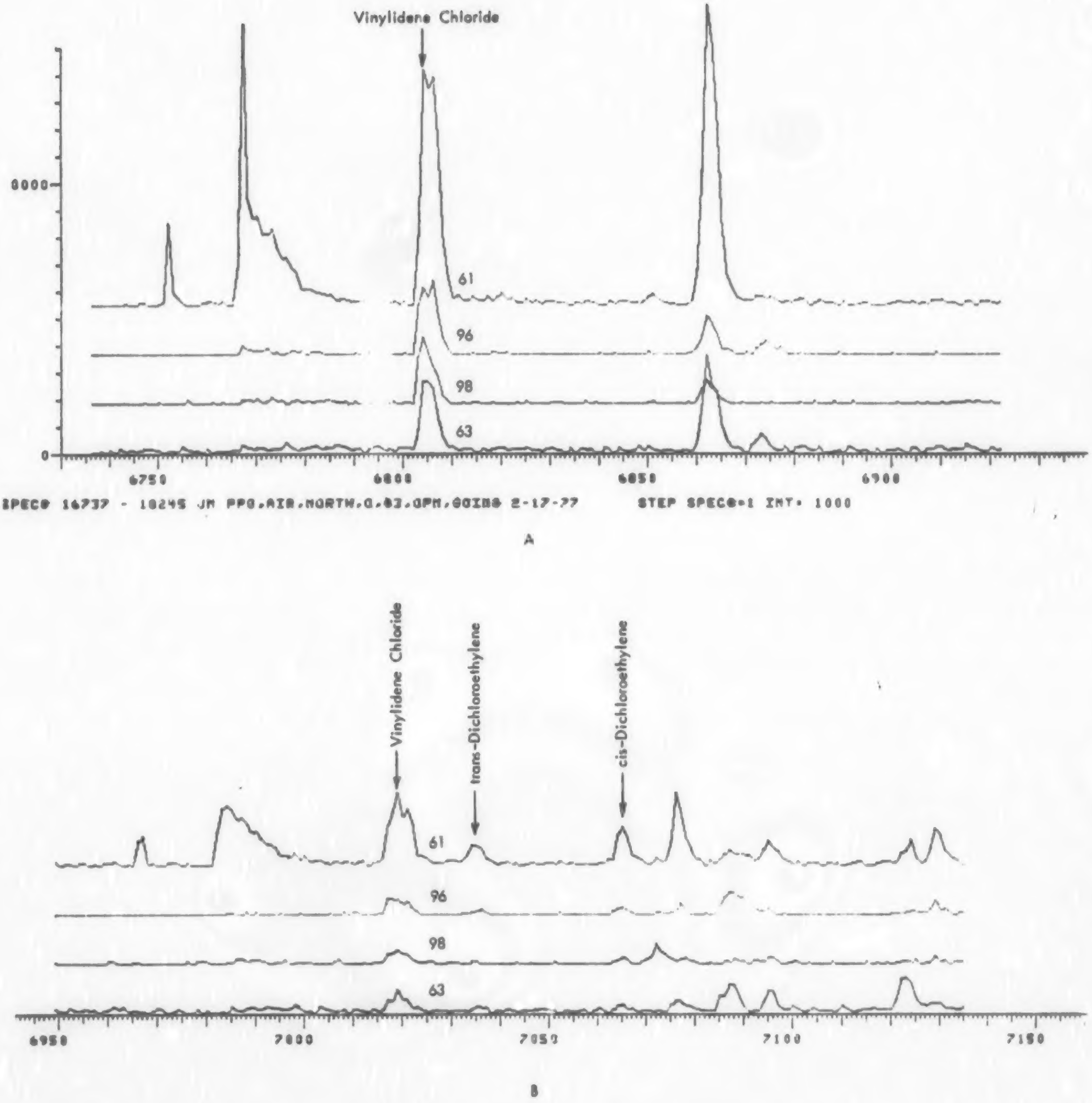


Figure 22. Extracted ion current plots for VDC - (A) PPG air sample No. 3, (B) PPG air sample No. 5

Table 35. SUMMARY OF GC-MS ANALYSIS OF PPG AIR SAMPLE NO. 3

Compound	m/e values	Intensity ratios	Spectrum no.	Observed intensity ratios	Conclusion	Product
Vinylidene chloride	61, 96, 98, 63	1.00:0.53:0.36:0.28	16804	1.00:0.29:0.27:0.27	Present	Yes
Carbon tetrachloride	119, 117, 121, 82	1.00:0.98:0.25:0.13	16842	1.0:1.0:-:-	Present	No
Chloroform	83, 85, 87, 47	1.00:0.55:0.07:0.14	16853	1.00:0.55:0.07:0.62	Present	No
Trichloroethylene	130, 132, 95, 97	1.00:0.95:0.85:0.59	16858	1.0:0.7:1.3:-	Present	Yes
Methyl chloroform	97, 99, 117, 119	1.00:0.62:0.19:0.19	16862	1.00:0.56:0.09:0.95	Present	Yes
Tetrachloroethylene	166, 164, 129, 131	1.00:0.78:0.75:0.65	16873	1.0:1.0:1.0:1.0	Present	Yes
Benzene	78, 79	1.00:0.06	16872	1.0:0.12	Present	No

Table 36. SUMMARY OF GC-MS ANALYSIS OF PPG AIR SAMPLE NO. 5

Compound	m/e values	Intensity ratios	Spectrum no.	Observed intensity ratios	Conclusion	Product
Vinylidene chloride	61, 96, 98, 63	1.00:0.53:0.36:0.28	17020	1.00:0.22:0.22:0.33	Present	Yes
trans-Dichloroethylene	61, 96, 98, 63	1.00:0.84:0.98:0.37	17035	1.0:0.2:0.2:0.2	Present (?)	No
Carbon tetrachloride	119, 117, 121, 82	1.00:0.98:0.25:0.13	17057	1.0:0.7:0.3:0.3	Present	No
cis-Dichloroethylene	61, 96, 98, 63	1.00:0.99:0.84:0.48	17065	1.00:0.2:0.2:0.2	Present (?)	No
Chloroform	83, 85, 87, 47	1.00:0.55:0.07:0.14	17069	1.00:0.56:0.08:0.56	Present	No
Trichloroethylene	130, 132, 95, 97	1.00:0.95:0.85:0.59	17072	1.0:0.9:1.0:0.8	Present	Yes
Methyl chloroform	97, 99, 117, 119	1.00:0.62:0.19:0.19	17076	1.00:0.75:0.16:-	Present	Yes
Tetrachloroethylene	166, 164, 129, 131	1.00:0.78:0.75:0.65	17087	1.0:1.0:1.0:1.0	Present	Yes
Benzene	78, 79	1.00:0.06	17086	1.0:0.1	Present	No
Toluene	91, 92, 65	1.00:0.51:0.10	17123	1.00:0.58:0.42	Present	No
1,1,2-Trichloroethane	83, 97, 85 99	1.00:0.98:0.64:0.62	17130	1.0:1.0:0.6:0.8	Present	No

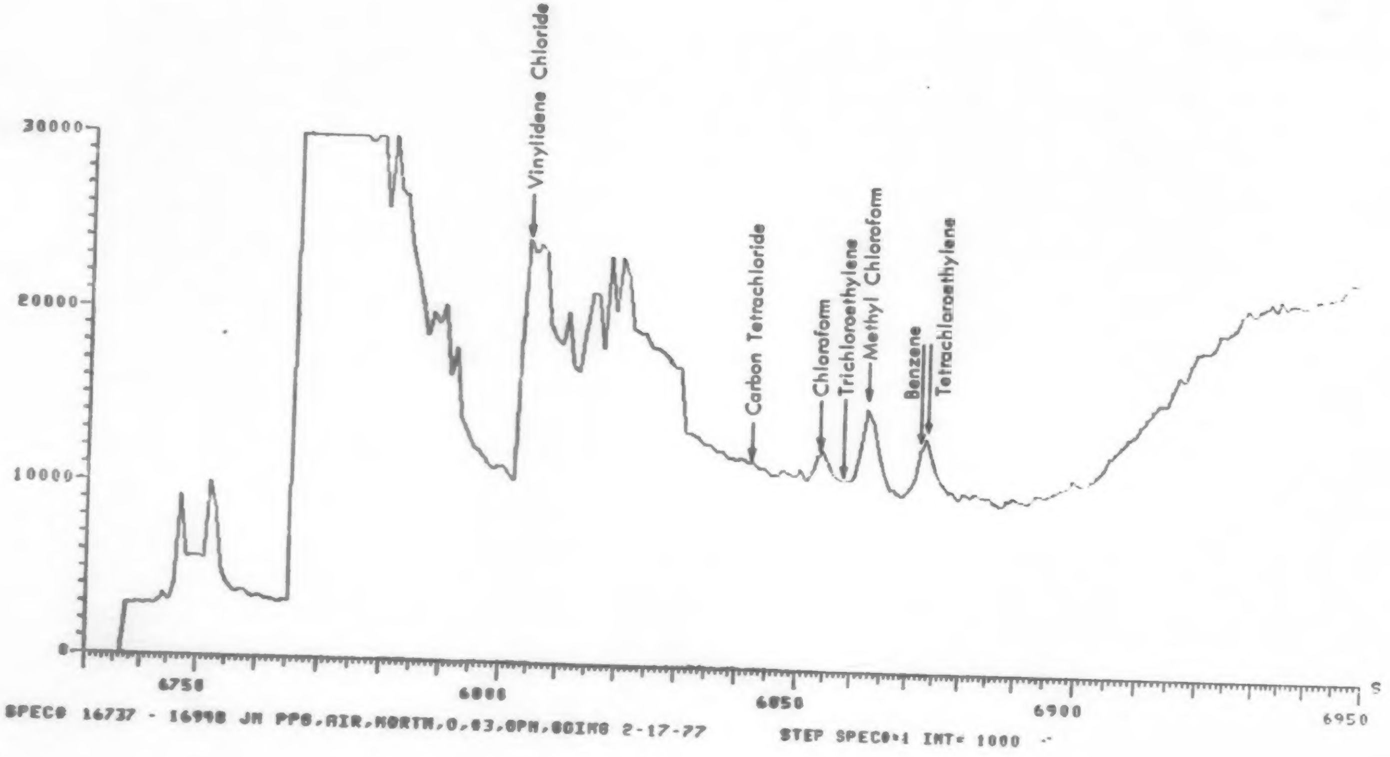


Figure 23. Sum plot of PPG air sample No. 3

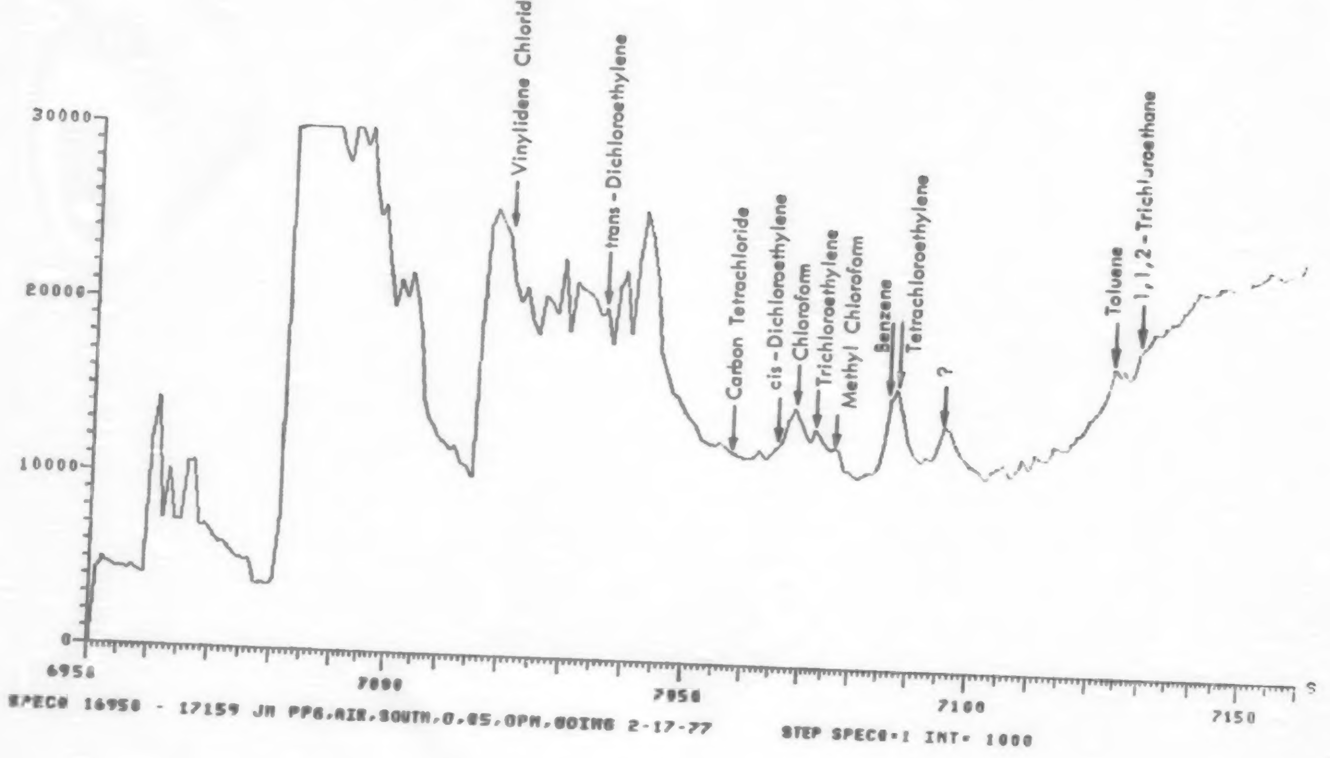


Figure 24. Sum plot of PPG air sample No. 5

Table 37. VDC CONCENTRATIONS IN WATER FROM PPG INDUSTRIES, LAKE CHARLES, LOUISIANA

Sample No.	Location	Volume analyzed	VDC found	µl/ℓ
W1	PPG Canal	1 ml	0.55 µg	550
W2	West Fork, Bayou d' Inde	10 ml	None	ND

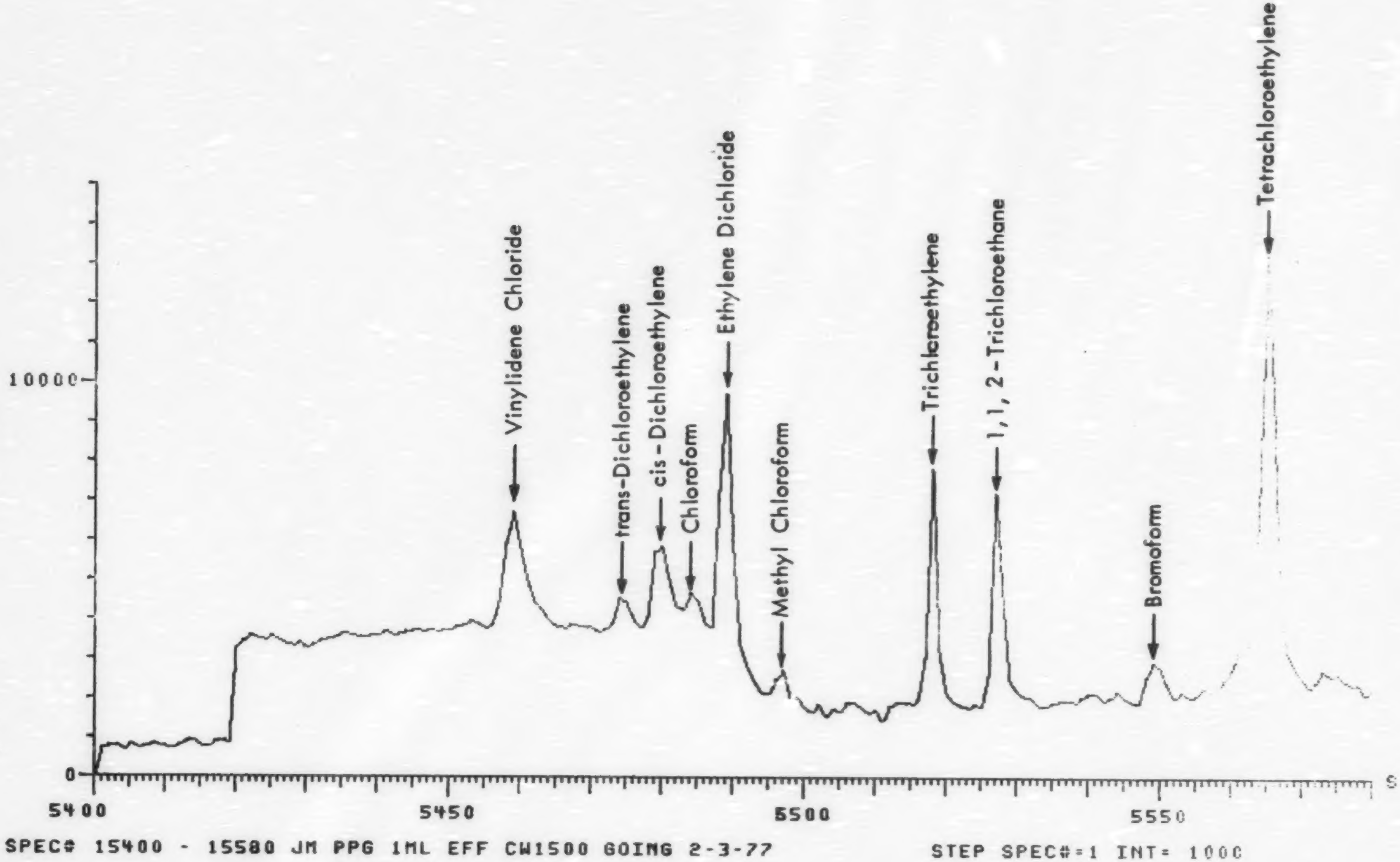


Figure 25. Sum plot of PPG water sample W-1

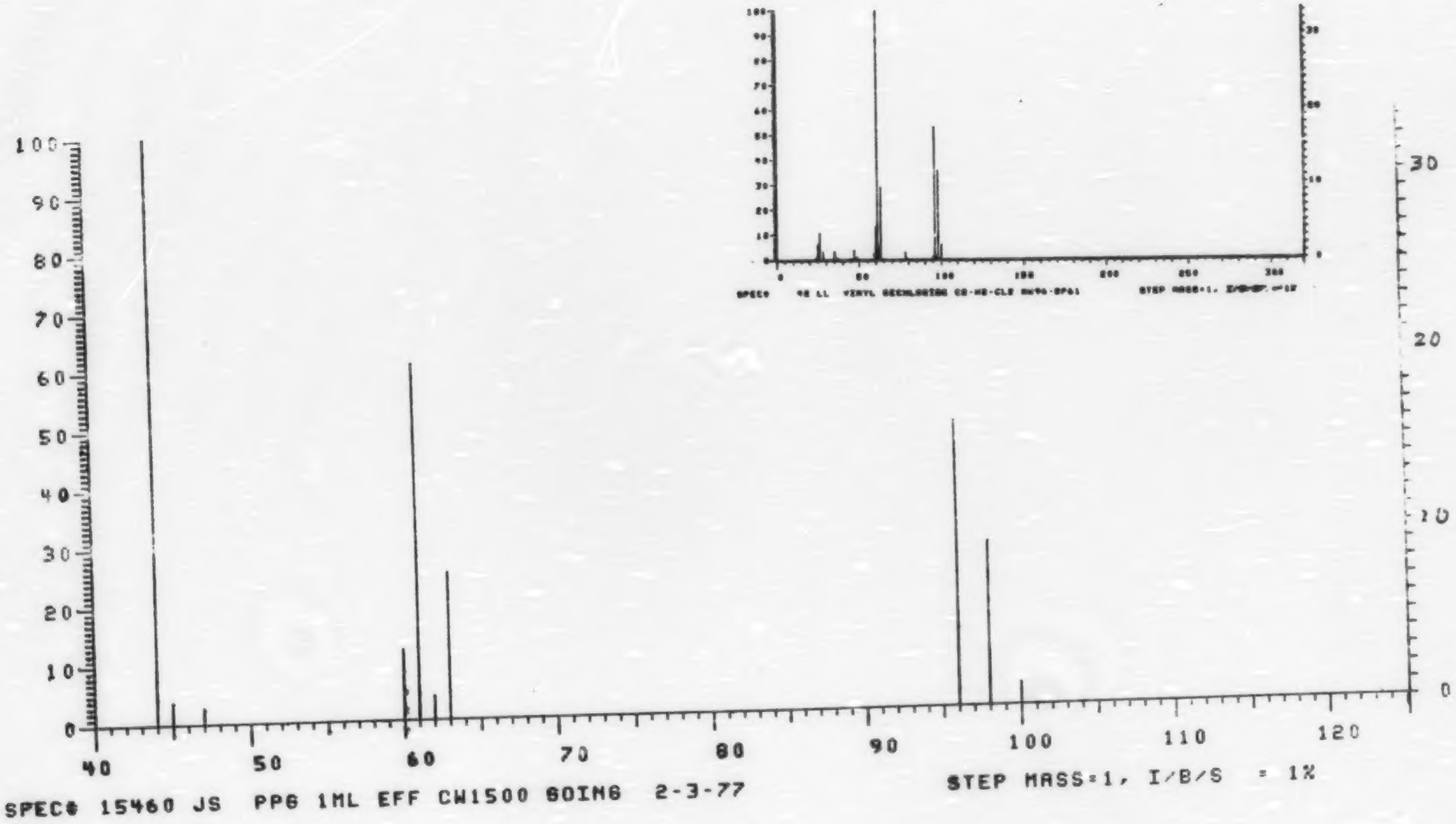


Figure 26. Mass spectrum of VDC in PPG water sample W-1

Identification of Other Compounds - Nine additional compounds were identified and have also been noted on the sum plot in Figure 25. As before, the presence (or absence) of a compound was determined using EICPs. Table 38 lists the compounds which were established as being present along with the ions monitored, the expected and actual intensity ratios and whether the compound is listed as a plant product. No estimate of concentration was made for any of the compounds. The following compounds were established by EICPs as being absent in the sample; vinyl chloride, methyl chloride, methylene chloride, ethyl chloride, 1,1-dichloroethane, carbon tetrachloride, 1,2-dichloropropane, benzene and toluene.

The upstream water sample, W2, was analyzed by GC/MS and found to be virtually free of any volatile components.

DIXICO, DALLAS, TEXAS

Field Sampling

A presampling survey was conducted on February 7, 1977, 1 day prior to sampling. The plant is located at 1300 South Polk Street, Dallas, Texas, in a residential area in the Oak Cliff subdivision of Dallas. There are no other manufacturing plants located in the immediate vicinity. No stacks were observed at the plant. Dixico uses barrier-coating latex and produces coated glassine.

The winds in this area generally blow from the south, south-southeast, and southeast in February and on an annual basis.

Field sampling was carried out during the 24-hr period from 0900 February 8, 1977, to 0900 February 9, 1977. Seven samplers were deployed at five sites located upwind, downwind, and laterally with respect to the plant. No water samples were collected.

Air Sampling - Air sampling was conducted using seven samplers located at five sites. Two charcoal tubes were used in series for each sampling train. The sites were established upwind of, lateral to, and downwind of the plant. Samplers were positioned at a height of 3 ft above ground level on public land such as right-of-ways. Samplers were located 0 and 0.1 miles from the plant perimeter. Locations of the five sites are shown in Figure 27. Site descriptions and air sampling data are given in Table 39. Duplicate samples were taken at the paired Sites 2 and 3, and 5 and 6.

Water Sampling - According to the Permits Section, U.S. EPA, Region VI, the Dixico plant has never requested a NPDES permit. Visual inspection of the plant likewise did not reveal any outfalls. Consequently, no water samples were collected from the Dixico plant.

Table 38. SUMMARY OF GC-MS ANALYSIS OF PPG WATER SAMPLE W-1

Compound	m/e values	Intensity ratios	Spectrum No.	Observed intensity ratios	Conclusion	Product	NPDES permit
Vinylidene chloride	61, 96, 98, 63	1.00:0.53:0.36:0.28	15459	1.00:0.66:0.39:0.24	Present	Yes	a/
trans-Dichloroethylene	61, 96, 98, 63	1.00:0.84:0.48:0.37	15474	1.00:1.00:0.50:0.38	Present	No	a/
cis-Dichloroethylene	61, 96, 98, 63	1.00:0.99:0.84:0.48	15480	1.00:0.77:0.59:0.36	Present	No	a/
Chloroform	83, 85, 47, 87	1.00:0.55:0.14:0.07	15484	1.00:0.67:0.08:0.08	Present	No	a/
Ethylene dichloride	62, 49, 64, 63	1.00:0.49:0.31:0.29	15489	1.00:0.73:0.28:0.28	Present	Yes	a/
Methyl chloroform	97, 99, 61, 117	1.00:0.62:0.36:0.19	15497	1.00:0.50:1.12:0.33	Present	Yes	a/
Trichloroethylene	95, 130, 132, 97	1.00:1.18:1.12:0.69	15518	1.00:0.93:1.02:0.69	Present	Yes	a/
1,1,2-Trichloroethane	83, 97, 85, 132	1.00:0.98:0.64:0.05	15527	1.00:1.02:0.68:0.11	Present	No	a/
Bromoform	173, 171, 175, 93	1.00:0.52:0.47:0.10	15549	1.00:0.46:0.47:0.25	Present	No	a/
Tetrachloroethylene	166, 164, 129, 131	1.00:0.78:0.75:0.85	15565	1.00:0.76:0.79:0.83	Present	Yes	a/

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a/ NPDES permit does not list specific compounds.

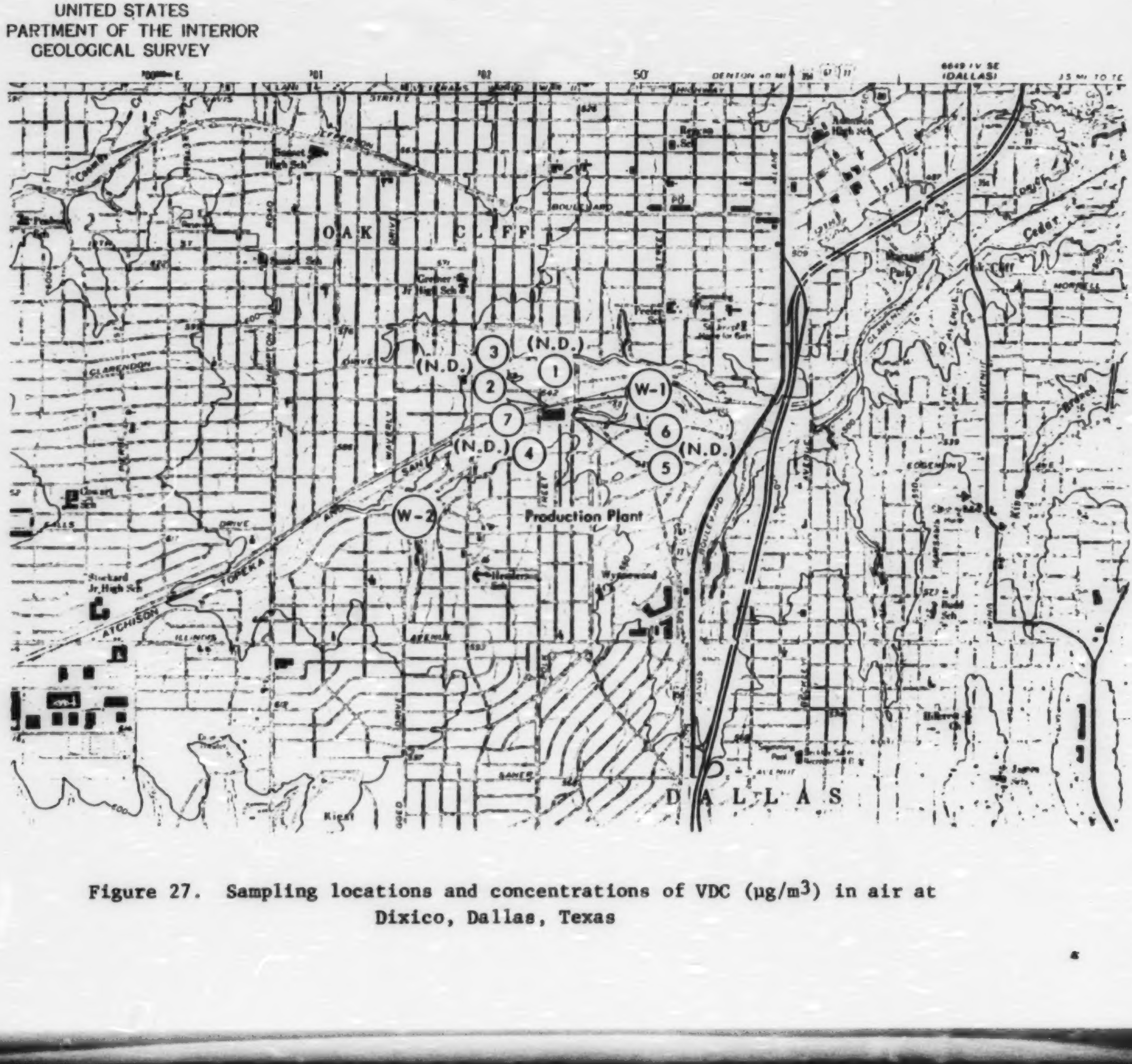
UNITED STATES
PARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
OAK CLIFF
DALLAS
Production Plant
1
(N.D.)
2
3
(N.D.)
4
(N.D.)
5
6
(N.D.)
7
W-1
W-2
ATCHISON
TOPEKA
SANTA
DENTON
Cedar

Figure 27. Sampling locations and concentrations of VDC (μg/m3) in air at Dixico, Dallas, Texas

Table 39. AIR SAMPLING DATA FOR DIXICO, DALLAS, TEXAS

Area	Sample no.	Exact location	Total sampling (hr)	Sampling rate (ℓ/min)	Total volume (m^3)	Sample height (ft)
North transect 0.1 mile	1	Corner, Polk St. and Nolte Dr.	23.6	0.982	1.390	3
North transect 0 mile	2	North property line, 20 ft east of Polk St.	23.6	1.069	1.512	3
North transect 0 mile	3	North property line, 20 ft east of Polk St.	23.6	1.057	1.496	3
South transect 0.1 mile	4	Corner, Polk St. and Elmdale Dr.	23.25	1.107	1.544	3
East transect 0 mile	5	Junction, Tyler St. and Vernon Ave.	23.6	0.573	0.811	3
East transect 0 mile	6	Junction, Tyler St. and Vernon Ave.	23.4	0.940	1.321	3
West transect 0.1 mile	7	South side Lebanon Ave., 0.1 mile west of Polk St.	23.25	0.875	1.220	3

Meteorological Conditions - A summary of the weather conditions existing during the air sampling period is given in Table 40.

Analysis of Air Samples

The results of the analysis of the air samples are listed in Table 41. No VDC was detected at any of the site locations shown in Figure 27. The wind rose pattern in Figure 28 shows that the sampling sites were correctly positioned to sample VDC if it had been present. Based upon the calibration curve for VDC, it can be estimated that the level of VDC in the air would have to be less than 1 $\mu g/m^3$.

No attempt was made to establish the identity of any other compounds in the air sampler.

Analysis of Water Samples

The Dixico plant did not have any known accessible outfalls; consequently, no water analyses were performed.

DEWEY AND ALMY, OWENSBORO, KENTUCKY

Field Sampling

A presampling survey was conducted on January 21, 1977. The plant is situated in Daviess County, Kentucky, along the southern bank of the Ohio River and about 3.2 miles east of the junction of US-60 and Kentucky Highway 212 off US-60. About 1.1 miles to the southwest is a power station operated by Owensboro Municipal Utilities. Stacks located at the plant are barely visible from the road and are no more than about 25 ft high.

The Dewey and Almy facility produces polybutadiene-styrene latex, polyvinyl acetate resins, polyvinyl chloride-vinylidene chloride copolymer resins, and styrene-butadiene copolymer resins.

Processed wastewater is discharged into the Ohio River at a point along the northeastern edge of the plant 35 ft out into the river and about 10 ft below the surface.

Winds in this area, according to data from Evansville, Indiana, blow from the northwest, west-northwest, and south-southwest in February and from the south-southwest, northwest, and southwest on an annual basis.

Field sampling was carried out during the 23-hr period from 1600 February 22, 1977 to 1500 February 23, 1977. Ten air samples were deployed at seven sites upwind, downwind, and laterally with respect to the plant. Water samples were taken upstream and downstream from the point of discharge.

Table 40. WEATHER CONDITIONS DURING SAMPLING AT DIXICO, DALLAS, TEXAS

Time	Wind Direction	Wind Speed (kts)	Precipitation
Tuesday, February 8			
0800	ESE	10	None
0900	SE	9	None
1000	SE	10	None
1100	SSE	6	None
1200	SE	9	None
1300	SSE	11	None
1400	W	6	None
1500	W	4	None
1600	SSW	10	None
1700	S	8	None
1800	SSW	8	None
1900	SSE	10	None
2000	SSE	12	None
2100	SSE	10	None
2200	SSE	10	None
2300	S	10	None
2400	SSE	8	None
Wednesday, February 9			
0100	S	9	None
0200	SSE	7	None
0300	SSE	6	None
0400	SSE	6	None
0500	SSE	4	None
0600	ESE	7	None
0700	SE	7	None
0800	SE	7	None
0900	SSE	6	None
1000	S	7	None

Table 41. VDC CONCENTRATIONS IN AIR SAMPLES FROM DIXICO, DALLAS, TEXAS

Sampling station	Sampling time	Volume (m^3)	Type of sample	VDC (μg)	Confirmation by bromination: Loss of VDC	Confirmation by bromination: Appearance of brominated VDC	Presence of chloroethane	VDC ($\mu g/m^3$)
1	0915-0850	1.39	Top charcoal Backup charcoal	ND[a]	-	-	-	ND
2	0905-0840	1.512	Top charcoal Backup charcoal	ND	-	-	-	ND
3	0905-0840	1.496	Top charcoal Backup charcoal	ND	-	-	-	ND
4	0950-0905	1.544	Top charcoal Backup charcoal	ND	-	-	-	ND
5	0925-0900	0.811	Top charcoal Backup charcoal	ND	-	-	-	ND
6	0935-0900	1.32	Top charcoal Backup charcoal	ND	-	-	-	ND
7	1000-0915	1.22	Top charcoal Backup charcoal	ND	-	-	-	ND
Blank No. 1	-	-	Top charcoal Backup charcoal	ND	-	-	-	ND
Blank No. 2	-	-	Top charcoal Backup charcoal	ND	-	-	-	ND

[a] ND = not detected.

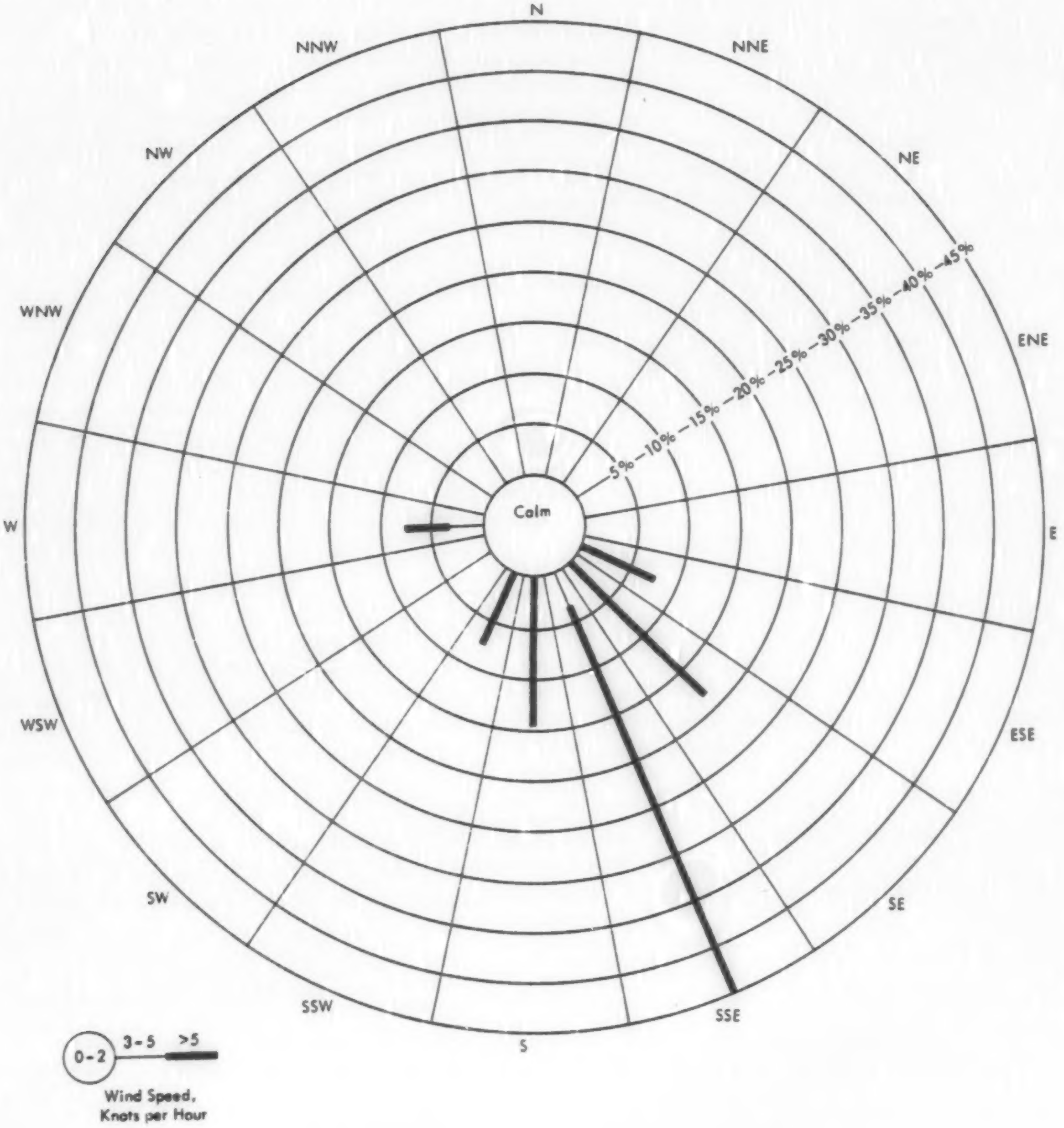

Figure 28. Wind patterns during sampling at Dixico, Dallas, Texas

Air Sampling - Air sampling was conducted using 10 samplers at seven sites. The sites were established upwind, laterally, and downwind of the plant with the majority being located downwind. Samplers were positioned at a height of 4 ft from ground level on public land such as right-of-ways and riverbanks. Sampling sites were located at approximately 0, 1/4, 1/3, and 2/3 mile from the plant perimeter. Locations of the 10 stations are shown in Figure 29. Site descriptions and air sampling data are given in Table 42. Sampling along the banks of the Ohio River was terminated early in the interest of safety.

Water Sampling - Two grab samples were obtained February 23, 1977. The upstream sample was taken from the Ohio River at a point approximately 2,000 ft upstream from the point of discharge and about 50 ft from the south bank. The downstream sample was taken approximately 2,000 ft downstream from the point of discharge and about 50 ft from the south bank. The locations are indicated in Figure 29.

Meteorological Conditions - A summary of the weather conditions existing during the air sampling period is given in Table 43.

Analysis of Air Samples

The results of the analysis of the charcoal tubes are listed in Table 44. No VDC was detected at any of the sites shown in Figure 29. The wind rose pattern in Figure 30 shows that the sampling Sites 1 and 8 were downwind of the plant during the sampling period. Based upon the calibration curve for VDC, it can be estimated that the level of VDC in the air was less than 1 $\mu g/m^3$.

The upwind and downwind samples did not show any notable difference when analyzed by GC using flame ionization detection. Therefore no GC/MS analysis of the air samples was performed to provide identification of other compounds.

Analysis of Water Samples

Water samples had been collected from the Ohio River approximately 2,000 ft upstream and downstream of the plant at a distance of 50 ft from the plant-side bank.

The samples were analyzed first by GC-FID, and no VDC was found. The downstream sample was then analyzed by GC/MS using the multiple ion selection (MIS) mode. Again, no VDC could be detected.

The upstream and downstream water samples were virtually identical by GC-FID analysis. Consequently no GC/MS analysis of the samples for components other than VDC was attempted.

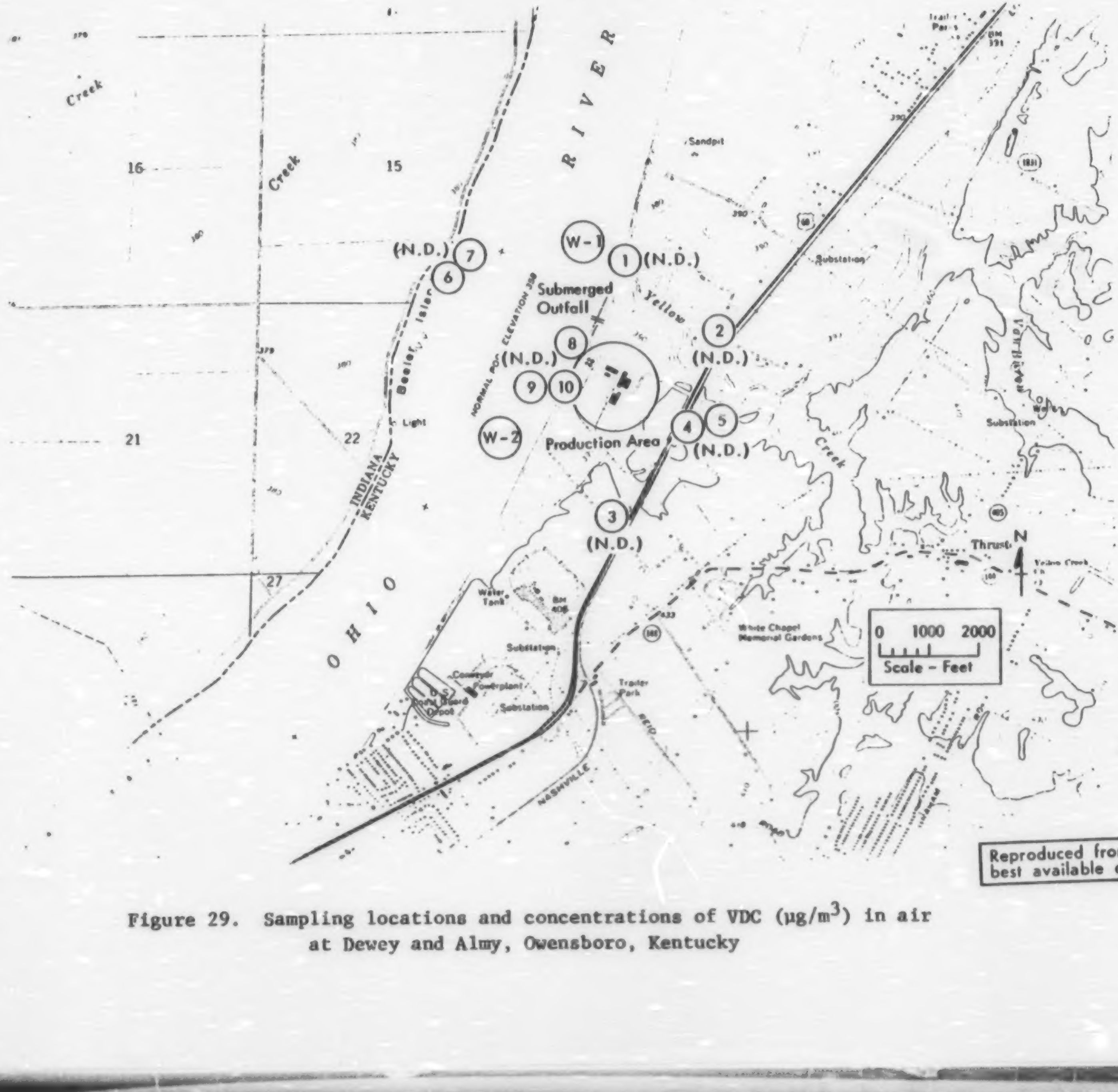
OHIO RIVER
INDIANA
KENTUCKY
Creek
Creek
16
15
21
22
27
Beelet Island
Light
NORMAL POOL ELEVATION 358
W-1
W-2
1 (N.D.)
2 (N.D.)
3 (N.D.)
4
5 (N.D.)
6
7 (N.D.)
8 (N.D.)
9
10
Submerged Outfall
Yellow
Creek
Production Area
Sandpit
Substation
Substation
Substation
Substation
Trailer Park
Trailer Park
Water Tank
Conveyor
Powerplant
U.S. Coast Guard Depot
Van Buren
White Chapel Memorial Gardens
Thruston
Yellow Creek
NASHVILLE
REID
N
0 1000 2000
Scale - Feet

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Figure 29. Sampling locations and concentrations of VDC (μg/m^3) in air at Dewey and Almy, Owensboro, Kentucky

Table 42. AIR SAMPLING DATA FOR DEWEY AND ALMY, OWENSBORO, KENTUCKY

Area	Sample no.	Exact location	Total sampling (hr)	Sampling rate (ℓ/min)	Total volume (m^3)	Sample height (ft)
North transect 0.75 mile	1	South bank of Ohio River, east of Yellow Creek	17.83	0.810	0.867	4
East-northeast transect 0.4 mile	2	Drive-in theater, 0.2 mile east of plant entrance	20.20	0.869	1.052	4
South transect 0.6 mile	3	Entrance to road, 0.3 mile west of plant entrance	19.83	0.649	0.772	4
East transect 0.3 mile	4	South side US-60 immediately south of plant	19.67	0.810	0.956	4
East transect 0.3 mile	5	South side US-60 immediately south of plant	19.67	0.809	0.955	4
West transect 0.6 mile	6	North side of Ohio River straight across from plant	16.17	0.650	0.631	4
West transect 0.6 mile	7	North side of Ohio River straight across from plant	16.17	0.830	0.805	4
West-northwest transect 0 mile	8	South side of Ohio River immediately west-northwest of plant	16.92	0.750	0.761	4
West transect 0 mile	9	South side of Ohio River immediately west of plant	17.5	0.720	0.756	4
West transect 0 mile	10	South side of Ohio River immediately west of plant	17.5	0.810	0.851	4

Table 43. WEATHER CONDITIONS DURING SAMPLING AT DEWEY AND ALMY, OWENSBORO, KENTUCKY

	Wind		
	Direction	Speed (kts)	Precipitation
Tuesday, February 22			
1200	SW	20	None
1300	SSW	21	None
1400	SW	20	None
1500	S	20	None
1600	SW	20	None
1700	SSW	13	None
1800	S	12	None
1900	S	12	None
2000	S	12	None
2100	S	12	None
2200	S	11	None
2300	S	12	None
2400	SSE	7	None
Wednesday, February 23			
0100	S	13	None
0200	S	15	None
0300	S	14	None
0400	S	12	None
0500	S	15	None
0600	S	12	None
0700	SSE	13	None
0800	SSE	13	None
0900	S	17	None
1000	S	17	None
1100	S	20	None
1200	S	18	None
1300	S	22	None
1400	S	23	None
1500	SSW	14	None
1600	SSE	13	None
1700	S	10	None

Table 44. VDC concentration in air samples from Dewey and Almy, Owensboro, Kentucky

Sampling station	Sampling time[a/]	Volume (m^3)	Type of sample	µg[b/]	Confirmation by bromination: Loss of VDC[b/]	Confirmation by bromination: Appearance of brominated VDC[c/]	Presence of chloroethane	µg/m^3
No. 1	1645-1035	0.867	Top charcoal	ND[d/]	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 2	1810-1429	1.052	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 3	1820-1410	0.772	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 4	1835-1415	0.956	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 5	1835-1415	0.955	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 6	1720-0850	0.631	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 7	1720-0850	0.805	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 8	1745-1040	0.761	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 9	1700-1030	0.756	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND

Table 44. (Concluded)

Sampling station	Sampling time[a]	Volume (m^3)	Type of sample	μg[b]	Loss of VDC[b]	Appearance of brominated VDC[c]	Presence of chloroethane	$\mu g/m^3$
No. 10	1700-1030	0.851	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
Blank No. 1			Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
Blank No. 2			Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND

---

[a] 2/22/77 to 2/23/77.
[b] Based on analysis on Durapak OPN column.
[c] Based on analysis on OV-101 column.
[d] Not detected.

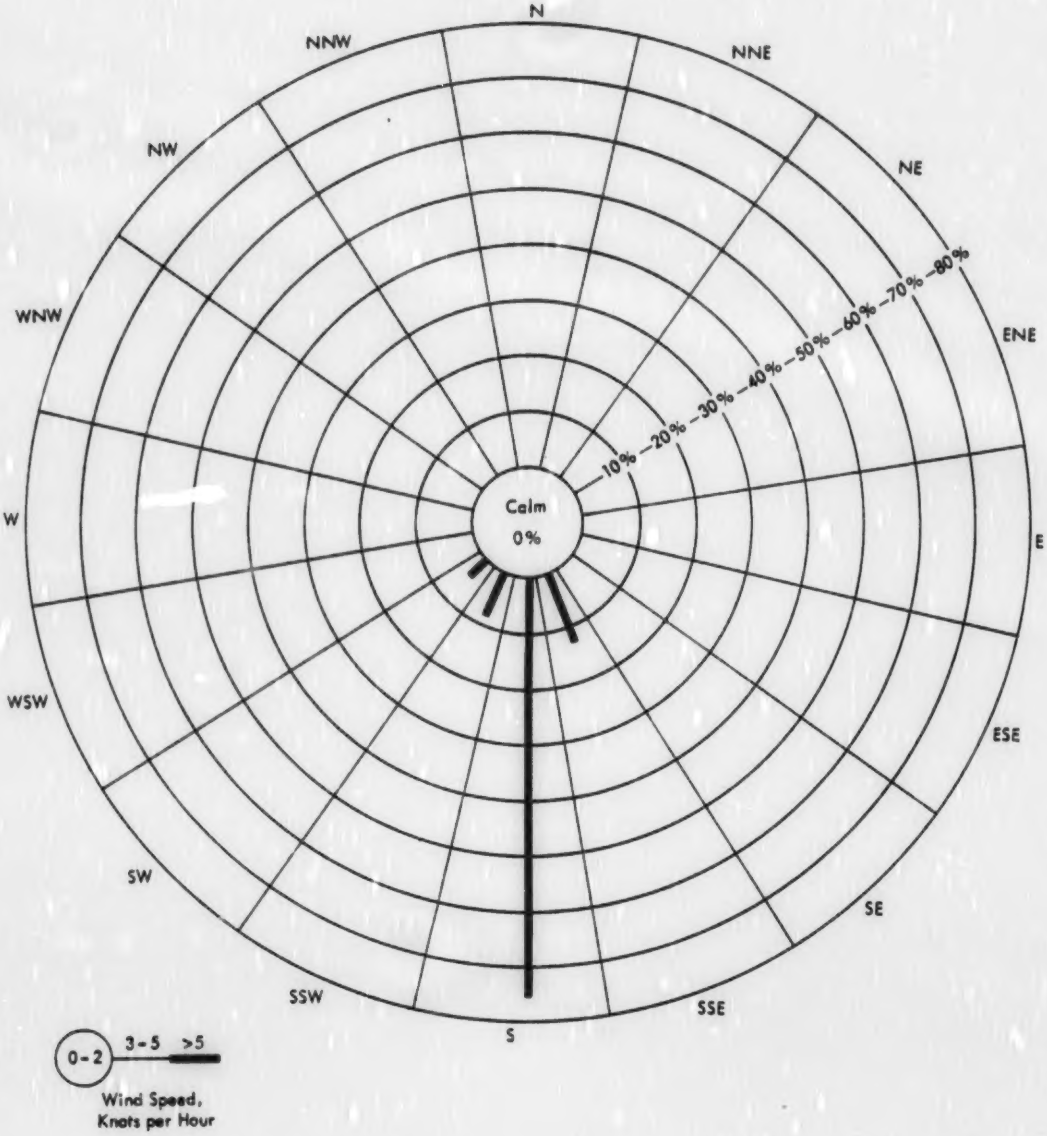

Figure 30. Wind Patterns During Sampling at Dewey and Almy

TENNESSEE EASTMAN, KINGSPORT, TENNESSEE

Field Sampling

A presampling survey was conducted on March 7, 1977. The Tennessee Eastman plant is located within the city limits of Kingsport, Tennessee, on the north bank of the south fork of the Holston River. The Holston Army Ammunition plant lies to the northwest. The Tennessee Eastman plant produces a large number of organic chemicals and modacrylic fibers. There are a series of seven discharge points from the plant into the Holston River including one from a water treatment facility.

Field Sampling was carried out during the 27-hr period from 9:00 a.m. March 8, 1977 to 12:00 p.m. March 9, 1977. Nine air samplers were deployed at nine sites upwind, downwind, and laterally with respect to the plant. Water samples were taken at four points upstream and downstream from the plant.

Air Sampling - Air sampling was conducted using nine samplers at nine sites. The sites were established upwind, laterally, and downwind of the plant. Samplers were positioned at a height of 4 ft above ground level on public land such as rights-of-way and schools. The sampling train consisted of two charcoal tubes in series. Sampling sites were all located within 1/4 mile of the plant perimeter. Sampling Site No. 1 was located within 15 ft of an existing, permanent air sampling station. Locations of the nine stations are shown in Figure 31. Site descriptions and air sampling data are given in Table 45.

Water Sampling - A total of 12 grab water samples were taken at four sites from each of three bridges on March 9, 1977. Samples W1 were taken from the bridge where Highway 93 crosses the south fork of the Holston River. These samples were upstream of all outfalls from the plant except outfall No. 008, which is scheduled to be discontinued by July 1, 1977, according to the Tennessee Eastman NPDES permit. Samples W2 and W3 were collected from the south and north end of the bridge, respectively, where South Wilcox Drive crosses the Holston River. This point is downstream of all outfalls except No. 002 from the wastewater treatment plant. Sample W2 was directly downstream of outfall No. 003. Sample W4 was taken from the C. P. Edwards Bridge about 1 mile downstream from the wastewater treatment facility. The locations of the outfalls and the points where the water samples were collected are shown in Figure 31.

Meteorological Conditions - A summary of the weather conditions existing during the air sampling period is given in Table 46.

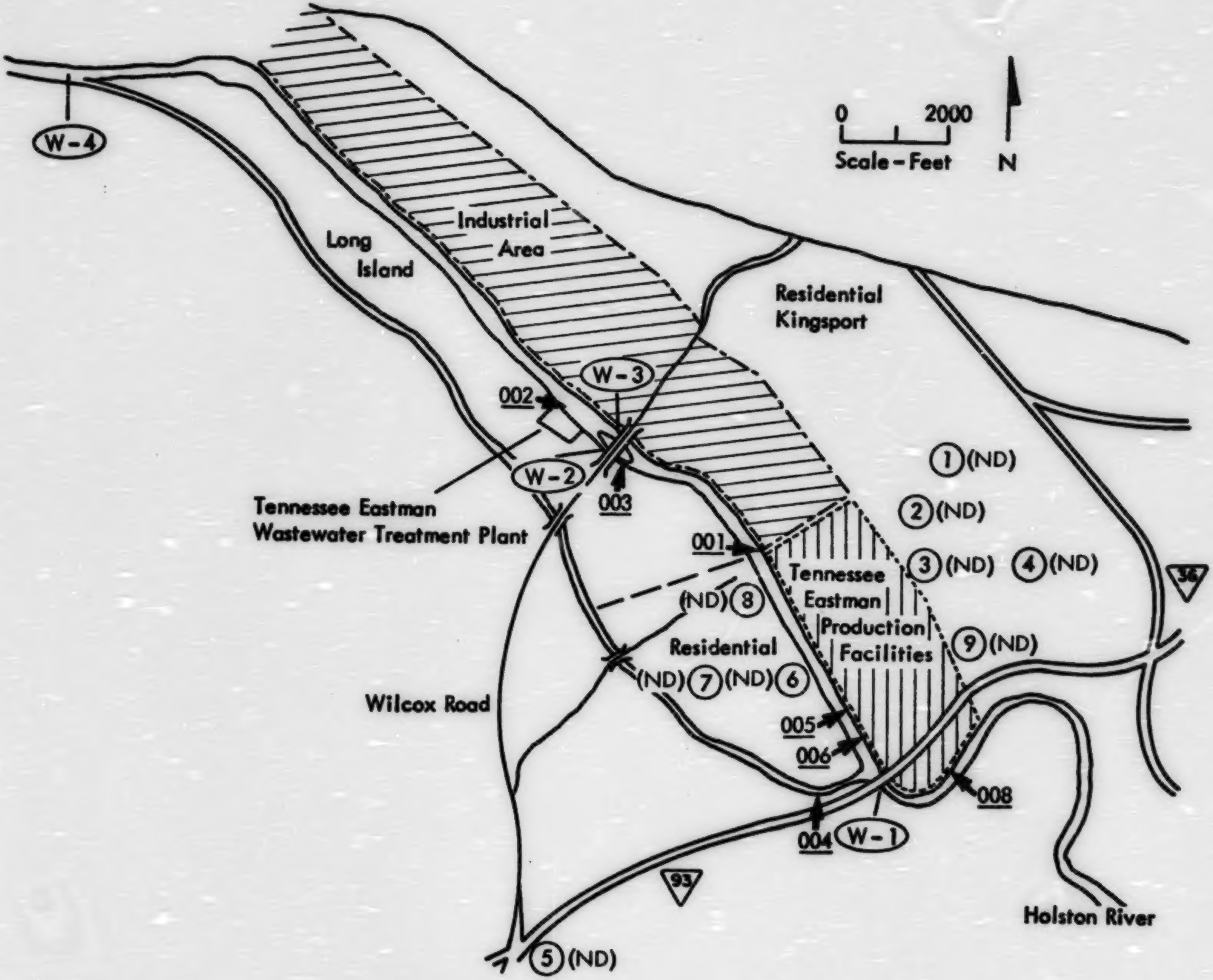
0
2000
Scale - Feet
N
W-4
Industrial
Area
Long
Island
Residential
Kingsport
W-3
002
W-2
003
Tennessee Eastman
Wastewater Treatment Plant
001
① (ND)
② (ND)
③ (ND)
④ (ND)
36
Tennessee
Eastman
Production
Facilities
(ND) ⑧
Residential
(ND) ⑦ (ND) ⑥
⑨ (ND)
Wilcox Road
005
006
008
004
W-1
93
Holston River
⑤ (ND)

Figure 31. Concentrations of VDC ($\mu g/m^3$) in Air at Nine Sampling Stations at Tennessee Eastman, Kingsport, Tennessee

Table 45. AIR SAMPLING DATA FOR TENNESSEE EASTMAN COMPANY, KINGSPORT, TENNESSEE

Area	Sample No.	Exact location	Total sampling (hr)	Sampling rate (ℓ/min)	Total volume (m^3)	Sample height (ft)
Northeast transect 0.5 mile	1	Fair Oaks St. & Sevier St.	25.2	0.87	1.31	4
Northeast transect 0.25 mile	2	Circle on Kenwood St.	24.9	1.00	1.50	4
Northeast transect 0 mile	3	Lincoln St. & Konnarock St.	25.8	0.87	1.31	4
East-northeast transect 0.25 mile	4	Sherwood St. & Sherwood Ext.	24.9	0.83	1.24	4
South transect 0.25 mile	5	Moreland Dr. & Highway 93	25.2	0.78	1.18	4
West-southwest transect 0 mile	6	Circle Dr. & Mason Rd.	25.3	0.95	1.45	4
West-southwest transect 0.25 mile	7	North side Long Island School	25.2	0.86	1.30	4
West transect 0 mile	8	Siler St. & River Rd.	25.5	0.91	1.40	4
East transect 0 mile	9	Lincoln St. & Highway 93	25.1	0.87	1.31	4

Table 46. WEATHER CONDITIONS DURING SAMPLING AT TENNESSEE EASTMAN, KINGSPORT, TENNESSEE

Time	Wind Speed (Kts.)	Wind Direction	Precipitation
March 8			
0900	3	NE	None
1000	3	ESE	None
1100	00	-	None
1200	6	SSW	None
1300	6	WSW	None
1400	8	WSW	None
1500	6	W	None
1600	9	W	None
1700	7	SW	None
1800	6	SSW	None
1900	4	SW	None
2000	00	-	None
2100	00	-	None
2200	00	-	None
2300	00	-	None
2400	3	ENE	None
March 9			
0100	00	-	None
0200	3	E	None
0300	3	ESE	None
0400	00	-	None
0500	00	-	None
0600	00	-	None
0700	3	ENE	None
0800	00	-	None
0900	4	E	None
1000	4	NE	None
1100	3	S	None
1200	4	SSE	None

Analysis of Air Samples

VDC Levels - The results of the analysis of the charcoal tubes by GC-FID are listed in Table 47. No VDC was detected at any of the site locations shown in Figure 31. The wind behavior for the day of sampling, shown as a wind rose in Figure 32, indicates that Stations 9, 3, and 4 were the downwind stations. The chromatograms of these samples, particularly No. 9, indicated the presence of significant concentrations of various components. Sample No. 9 was considered to be the most likely one to contain any VDC and consequently was analyzed by GC/MS. The presence of VDC was tested by an EICP using the ions 61, 96, 98, and 63. The EICP for Sample No. 9 is shown in Figure 33. The peak maxima for the four selected ions occur at the appropriate time in the sample chromatogram and were absent in the field blank. When compared to a standard, the results suggest that less than 1 μg of VDC was present in the 1.31 m^3 air sample. Since this was the closes downwind sample, the level of VDC in the upwind and farther downwind samples appeared to be negligible.

Identification of Other Components - All air samples, when analyzed by GC-FID, showed the presence of several other components at significant levels, although the highest levels were at the downwind stations.

As previously mentioned, Sample No. 9 was analyzed by GC/MS. Initially, selected ion plots were used to establish the presence or absence of specific compounds.

Manual interpretation as well as a Cyphernetic search were also used. Table 48 lists all the compounds tentatively identified and the basis of the identification. The identified compounds are also noted on the sum plot shown in Figure 34.

The two peaks after VDC appear to be structural isomers of hexane. The next peak was matched by Cyphernetics computer search with cyclohexane and 2-hexene, having similar indices of 0.735 and 0.728, respectively. The next cluster of peaks was shown by a series of selected ion and limited mass range plots to be composed of five to six unresolved peaks. Identification of the major components was rendered impossible due to the overlapping of the peaks and the fact that most of the major fragment ions had saturated the detector. The unsubtracted mass spectra have the appearance of being C-6 methyl ketones. Tennessee Eastman lists 2-heptanone, methyl n-butyl ketone, methyl n-heptal ketone, methyl isoamyl ketone, and methyl isobutyl ketone as company products.

Table 47. VDC CONCENTRATIONS IN AIR SAMPLES FROM TENNESSEE EASTMAN, KINGSPORT, TENNESSEE

Sampling station	Sampling time[a]	Volume (m^3)	Type of sample	µg[b]	Loss of VDC[b]	Appearance brominated VDC[c]	Presence of chloroethane	$\mu g/m^3$
No. 1	1020-1121	1.31	Top charcoal	ND[d]	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 2	1030-1125	1.50	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 3	1013-1118	1.31	Top charcoal	ND	--	--	--	ND
			Backup charcoal	ND	--	--	--	ND
No. 4	1037-1130	1.24	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 5	1000-1111	1.18	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 6	0927-1048	1.45	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 7	0945-1057	1.30	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 8	0912-1042	1.40	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 9	1008-1115	1.31	Top Charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
Blank	--	--	Top charcoal	ND	--	--		
			Backup charcoal	--	--	--		

---

[a] 3/8/77 to 3/9/77.

[b] Based on analysis using Durapak OPN column.

[c] Based on analysis using OV-101 column.

[d] Not detected.

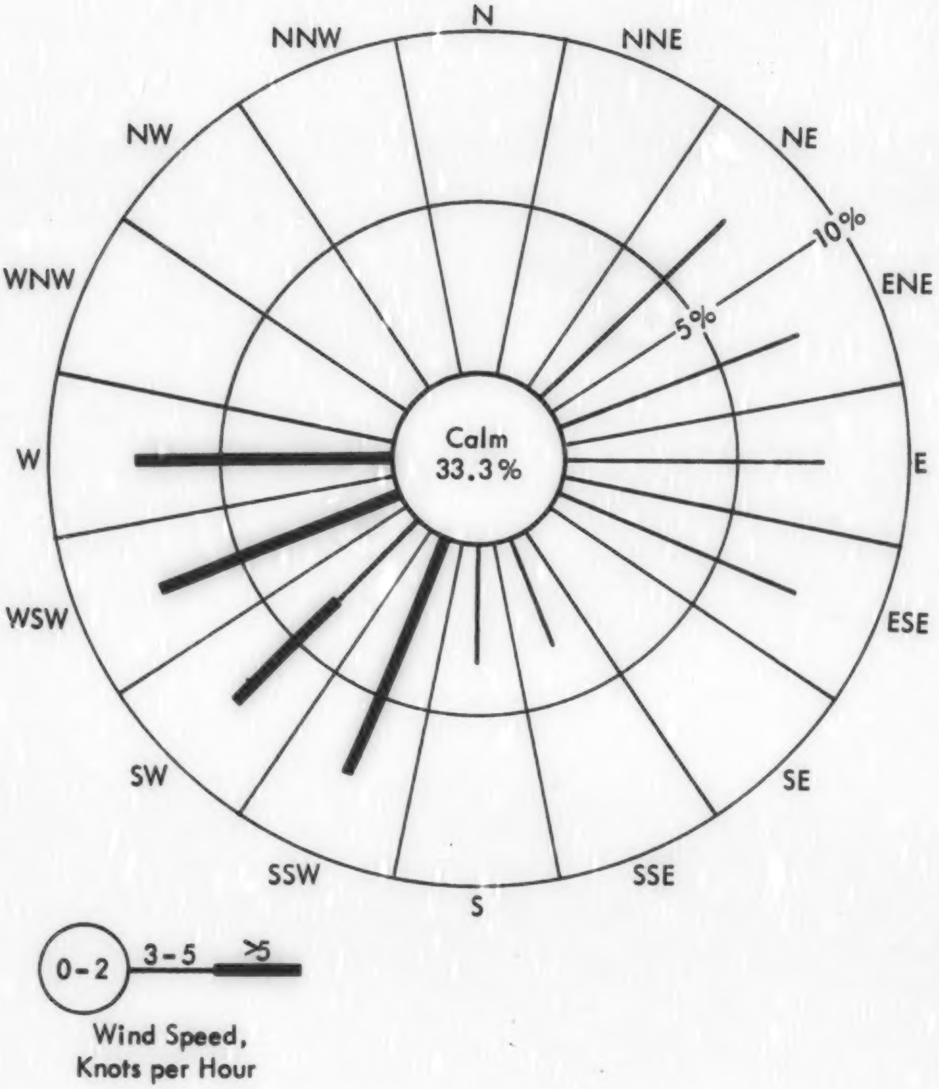

Figure 32. Wind Patterns During Sampling at Tennessee Eastman

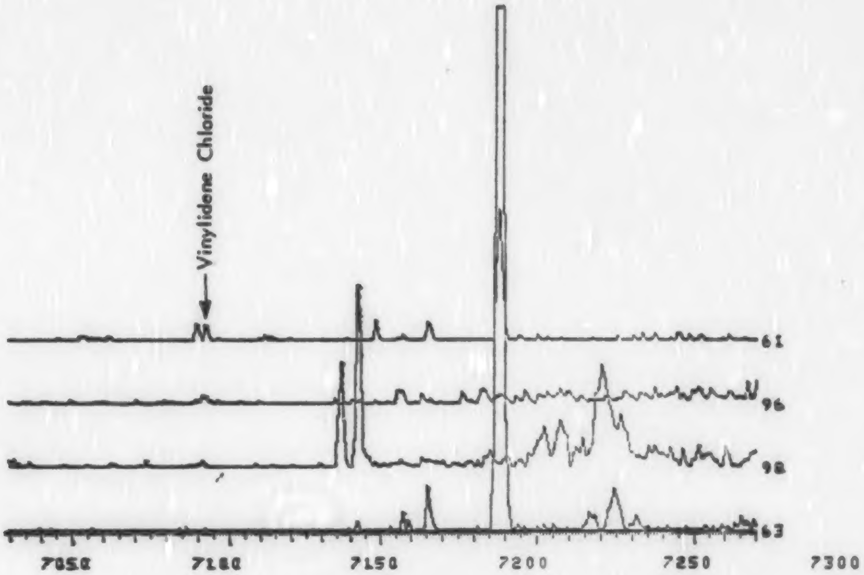

Figure 33. Extracted ion current plot of Tennessee Eastman air sample No. 9 for VDC

Table 48. SUMMARY OF GC/MS ANALYSIS OF TENNESSEE EASTMAN AIR SAMPLE NO. 9

Compound	Basis of identification	m/e values	Intensity ratios	Spectrum number	Observed intensity ratios	Product or known use
Vinylidene chloride	SIP[a]	61, 96, 98, 63	1.00:0.53:0.36:0.28	7092	b/	Yes
Hexane isomer	MAN[c]	-	-	7112	-	No
Hexane isomer	MAN	-	-	7116	-	No
Cyclohexane or 2-hexene	CYP[d]	-	-	7121	-	No
Carbon tetrachloride	SIP	119, 117, 121, 82	1.00:0.98:0.25:0.13	7129	1.0:1.0:0.2:0.2	No
C-6 methyl ketones	MAN (?)	-	-	7138,7142	-	Yes
Benzene	SIP	52, 51, 50, 79[e]	1.00:0.71:0.59:0.35	7156	1.00:0.81:0.65:0.27	No
Toluene	SIP	91, 92, 65, 63	1.00:0.51:0.10:0.04	7187	All peaks saturated	No

a/ SIP = Selected ion plots.
b/ Peaks were too small to make a meaningful measurement.
c/ MAN = Manual interpretation of mass spectrum.
d/ CYP = Identified by computer search of Cyphernetics file.
e/ m/e 78 peak was saturated and could not be used.

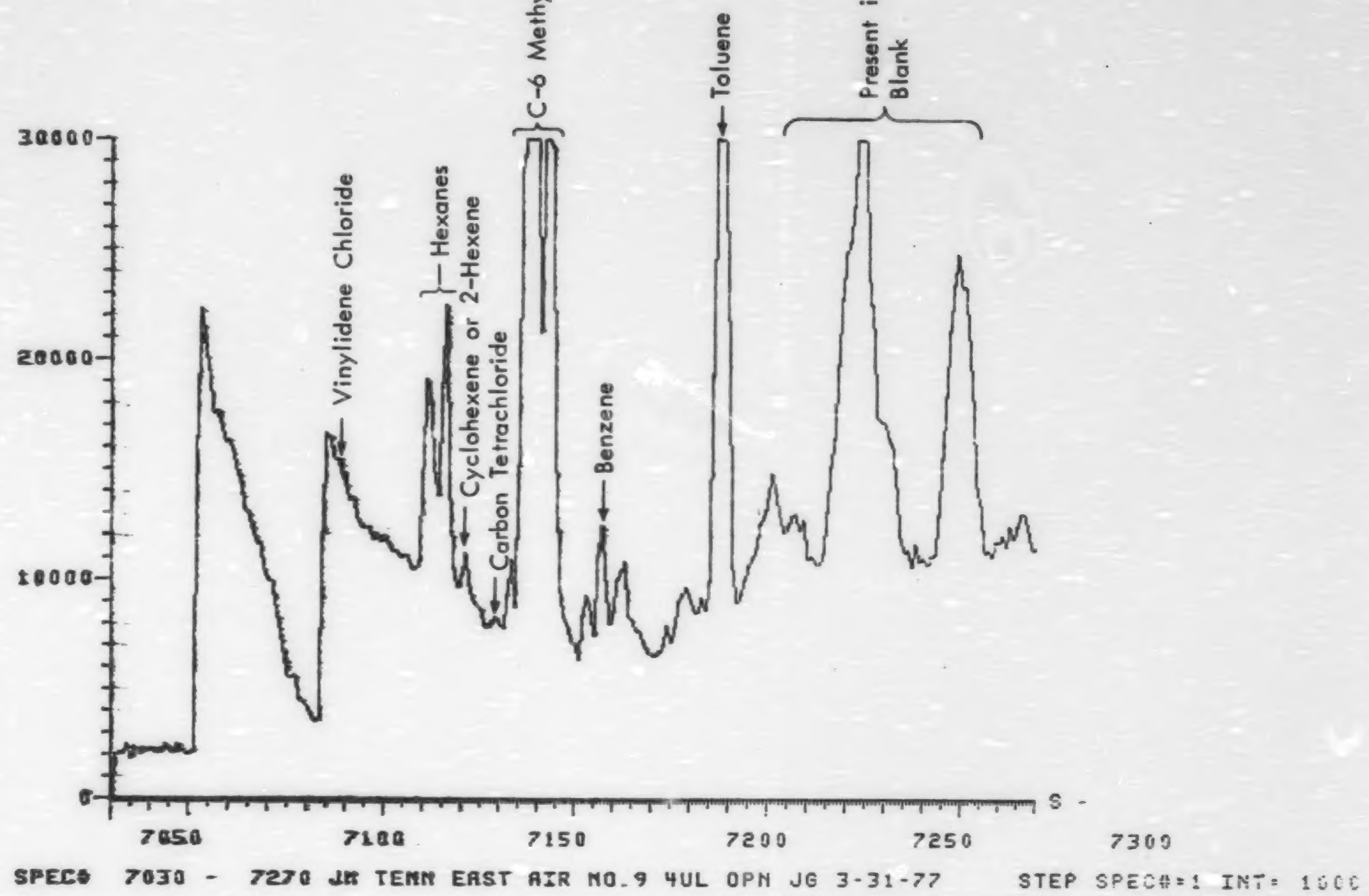

Figure 34. Sum plot of Tennessee Eastman Air Sample No. 9

Analysis of Water Samples

VDC Levels - The water samples collected at four points from the Holston River were analyzed for VDC by GC using flame ionization detection. The results are summarized in Table 49.

The only sample where VDC was detected by FID was W2 which had been collected immediately downstream of outfall No. 003. Sample W1 was contaminated during analysis. The samples were analyzed by GC/MS using the multiple ion scan mode and VDC was found in Samples W2 and W4. Identity was confirmed by matching retention times and intensity ratios for the peaks monitored with those of a standard. The peak ratios are included in Table 49. No attempt was made to quantify the level of VDC by GC/MS although the samples were estimated to contain less than 1 μg/liter VDC.

Identification of Other Components - The upstream and downstream water samples did not show any notable differences when analyzed by GC with flame ionization detection. Therefore no GC/MS analyses of the water samples for any other components were performed.

DOW CHEMICAL, MIDLAND, MICHIGAN

Field Sampling

A presampling survey was conducted on March 21, 1977. The Dow Chemical plant is located in Midland Township, Midland County, Michigan, immediately south of the city of Midland, Michigan. The Tittabawassee River runs through the plant complex. The city of Midland, Michigan, is on the north side of the plant. To the east is a facility of Dow-Corning, to the south is a nuclear power plant under construction, and to the west is a rural area. The Dow Chemical plant produces a large number of organic chemicals and Saran Wrap. There are a series of five discharge points along the Tittabawassee River.

The winds in this area generally blow from the west-southwest, west, and northwest during the month of March and from the west-southwest, southwest, and west on an annual basis.

Field sampling was carried out during the 30-hr period from 9:00 a.m. March 22, 1977 to 3:00 p.m. March 23, 1977. Thirteen air samplers were deployed at 13 sites upwind, downwind, and laterally with respect to the plant. Water samples were taken at three points upstream and downstream from the plant.

On March 22, 1977, a luncheon meeting was held with Diane M. Carlson of the Michigan Department of Natural Resources, after which Ms. Carlson was shown an air sampler. Ms. Carlson then accompanied the sampling crew

Table 49. VDC CONCENTRATIONS IN WATER FROM TENNESSEE EASTMAN', KINGSPORT, TENNESSEE

Sample No.	Volume analyzed	VDC Found		Level
		GC-FID	GC-MS-MIS (peak ratios)[a]	
W-1	10 ml	ND[b]	ND	ND
W-2	10 ml	1 μg	Yes [1.00:0.71:0.55:0.39]	~ 1 ppb
W-3	10 ml	ND	NA	ND
W-4	10 ml	ND	Yes [1.00:0.63:0.42:0.33]	< 1 ppb

---

[a] Peak intensities for m/e 61, 96, 98, 63, for standard were 1.00:0.67:0.42:0.38.

[b] ND = Not detected.

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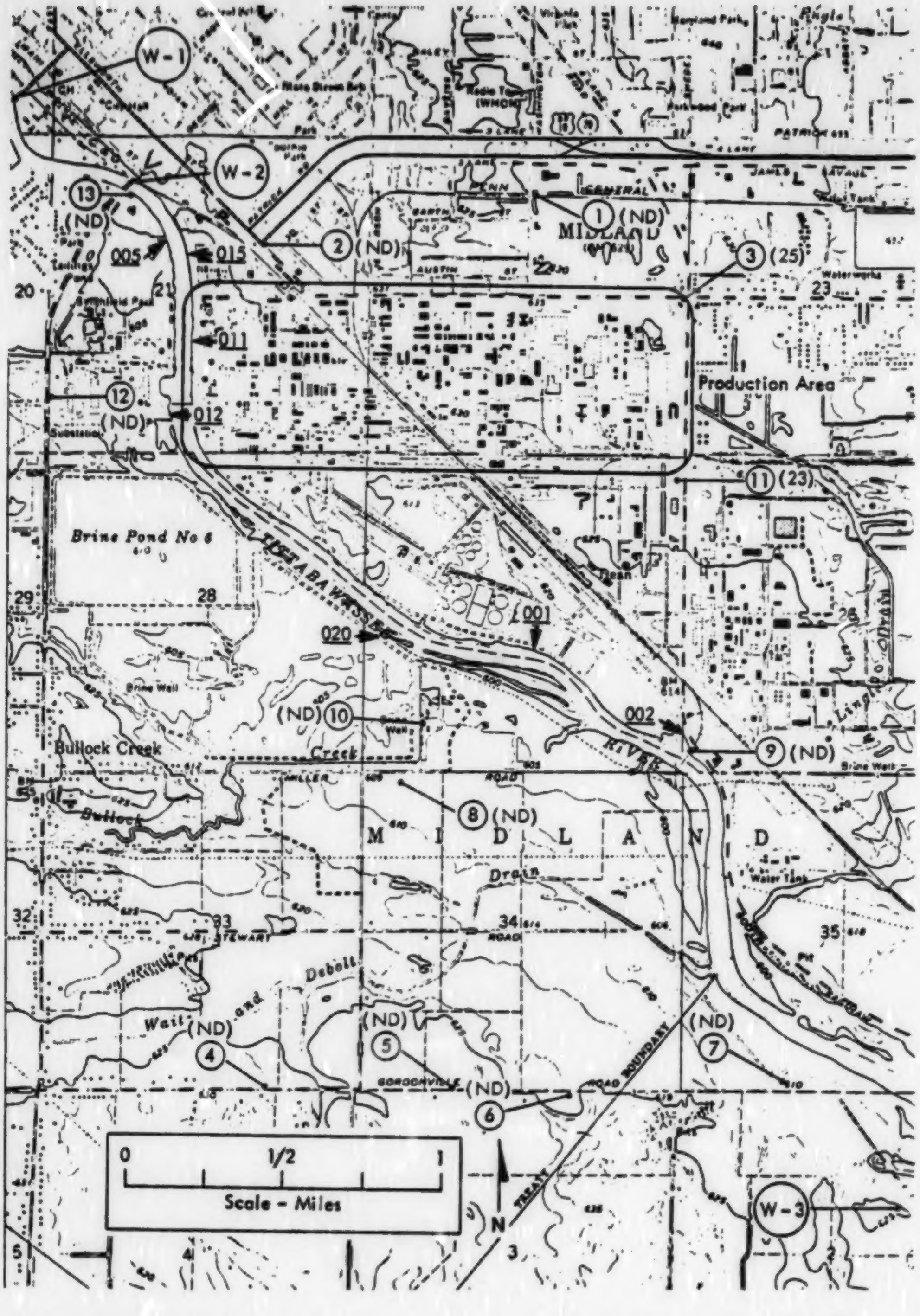
W-1
W-2
13
(ND)
005
015
2 (ND)
1 (ND)
MIDLAND
3 (25)
Waterworks
23
20
21
011
12
(ND)
012
Production Area
11 (23)
Brine Pond No 6
29
28
020
001
(ND) 10
002
9 (ND)
Bullock Creek
Creek
8 (ND)
M I D L A N D
Drain
32
33
34
35
STEWART
ROAD
Debolt
Wait
and
(ND)
4
(ND)
5
(ND)
7
(ND)
6
GORDONVILLE
0
1/2
1
Scale - Miles
N
W-3
5
4
3
2

Figure 35. Sampling locations and concentrations of VDC ($\mu g/m^3$) in air at Dow Chemical, Midland, Michigan

Table 50. AIR SAMPLING DATA FOR DOW CHEMICAL, MIDLAND, MICHIGAN

Area	Sample No.	Exact location	Total sampling (hr)	Sampling rate (liters/min)	Total volume (m^3)	Sample height (ft)
North transect 0.25 mile	1	Washington St. & Penn Central Tracks	22.9	0.95	1.301	4
Northwest transect 0 mile	2	Ellsworth St. & Lyons St.	23.1	0.92	1.272	4
Northeast transect 0 mile	3	Bay City Rd. & Saginaw Rd.	21.8	1.04	1.363	4
South-southwest transect 1 mile	4	0.7 miles east of Poseyville Rd. on Gordonville Rd.	23.4	0.90	1.268	4
South transect 1 mile	5	1.3 miles east of Poseyville Rd. on Gordonville Rd.	23.5	0.85	1.201	4
South-southeast transect 1 mile	6	1.7 miles east of Poseyville Rd. on Gordonville Rd.	23.5	0.80	1.134	4
Southeast transect 1 mile	7	Gordonville Rd. & Tittabawassee River	23.6	0.67	0.957	4
Southwest transect 1 mile	8	Little League baseball field on E. Miller Rd.	23.3	0.73	1.020	4
Southeast transect 0.25 mile	9	Saginaw Rd. & Chesapeake & Ohio Tracks	23.7	0.68	0.970	4
Southwest transect 0.75 mile	10	Road to Bechtel Power Plant	23.2	0.91	1.264	4
East transect 0 mile	11	0.4 miles south of Bay City Rd. on Saginaw Rd.	23.9	0.89	1.279	4
West transect 0 mile	12	1.2 miles north of E. Miller Rd. on Poseyville Rd.	23.2	0.92	1.279	4
Northwest transect 0 mile	13	Poseyville Rd. & Tittabawassee River	23.1	0.78	1.077	4

Table 51. WEATHER CONDITIONS DURING SAMPLING AT DOW CHEMICAL, USA, MIDLAND, MICHIGAN

Time	Wind Speed (Kts.)	Wind Direction	Precipitation
March 22			
0900	17	N	None
1000	17	NNW	None
1100	16	N	None
1200	20	N	None
1300	18	N	None
1400	13	N	None
1500	17	NNW	None
1600	13	WNW	None
1700	17	NNW	None
1800	13	WNW	None
1900	10	NW	None
2000	7	NW	None
2100	7	WNW	None
2200	7	W	None
2300	7	W	None
2400	7	W	None
March 23			
0100	10	WSW	None
0200	7	W	None
0300	7	WSW	None
0400	6	WSW	None
0500	7	SSW	None
0600	7	SSW	None
0700	7	SSW	None
0800	11	SW	Lt. Snow
0900	12	SW	Lt. Snow
1000	13	SSW	Lt. Snow
1100	9	SSW	Lt. Snow

Table 52. VDC CONCENTRATIONS IN AIR AT DOW CHEMICAL, MIDLAND, MICHIGAN

Sampling station	Sampling time[a]	Volume (m^3)	Type of sample	μg[b]	Confirmation by bromination: Loss of VDC[b]	Confirmation by bromination: Appearance of brominated VDC[c]	Presence of chloroethane	μg/m^3
No. 1	1135-1030	1.301	Top charcoal	ND[d]	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 2	1120-0025	1.272	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 3	1150-0937	1.363	Top charcoal	34	Yes	Yes	No	25
			Backup charcoal	ND	--	--	--	ND
No. 4	1035-1000	1.268	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 5	1026-0957	1.201	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 6	1022-0953	1.134	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 7	1012-0950	0.957	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 8	1050-1006	1.020	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 9	1003-0945	0.970	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 10	1059-1010	1.264	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND

Table 52. (Concluded)

Sampling station	Sampling time[a]	Volume (m^3)	Type of sample	µg[b]	Confirmation by bromination		Presence of chloroethane	µg/m^3
					Loss of VDC[b]	Appearance of brominated VDC[c]		
No. 11	0949-0941	1.279	Top charcoal	29	Yes	Yes	No	23
			Backup charcoal	ND	--	--	--	ND
No. 12	1106-1016	1.279	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
No. 13	1113-1019	1.077	Top charcoal	ND	--	--	--	ND
			Backup charcoal	--	--	--	--	ND
Blank	--	--	Top charcoal	ND	--	--	--	ND
			Backup charcoal	ND	--	--	--	ND

---

[a] 3/22/77 to 3/23/77.
[b] Based on analysis using Durapak OPN column.
[c] Based on analysis using OV-101 column.
[d] ND = Not detected.

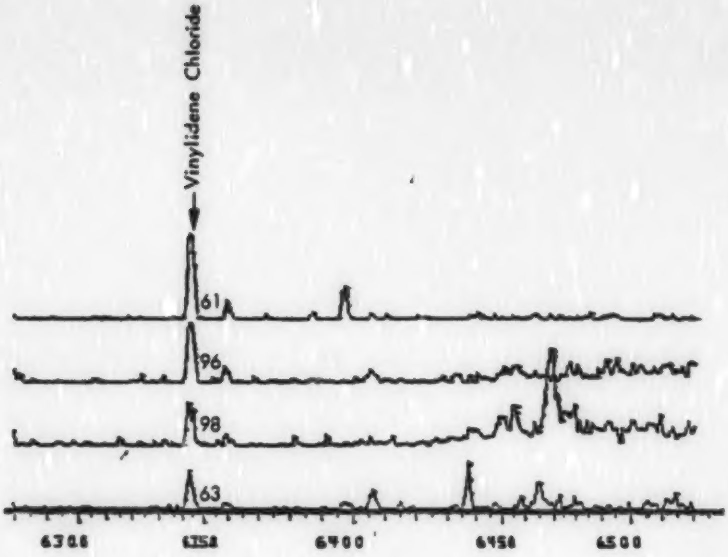

Figure 36. Extracted ion current plot of Dow Chemical air sample No. 3 for VDC

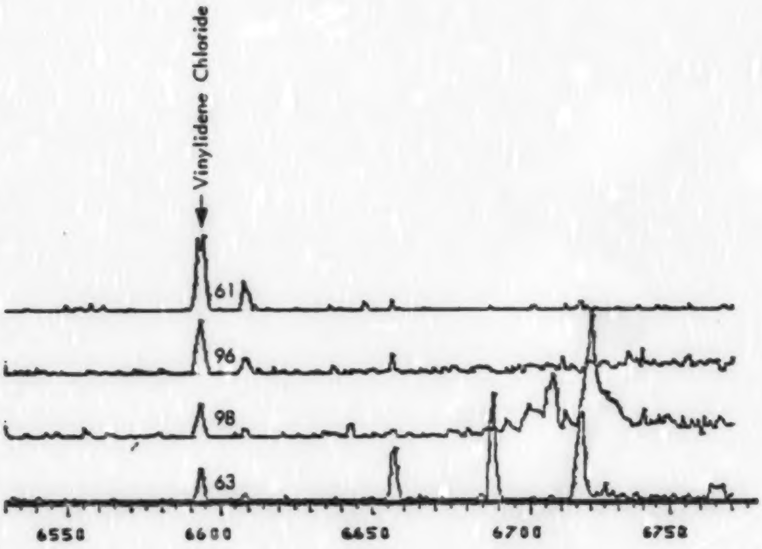

Figure 37. Extracted ion current plot of Dow Chemical air sample No. 11 for VDC

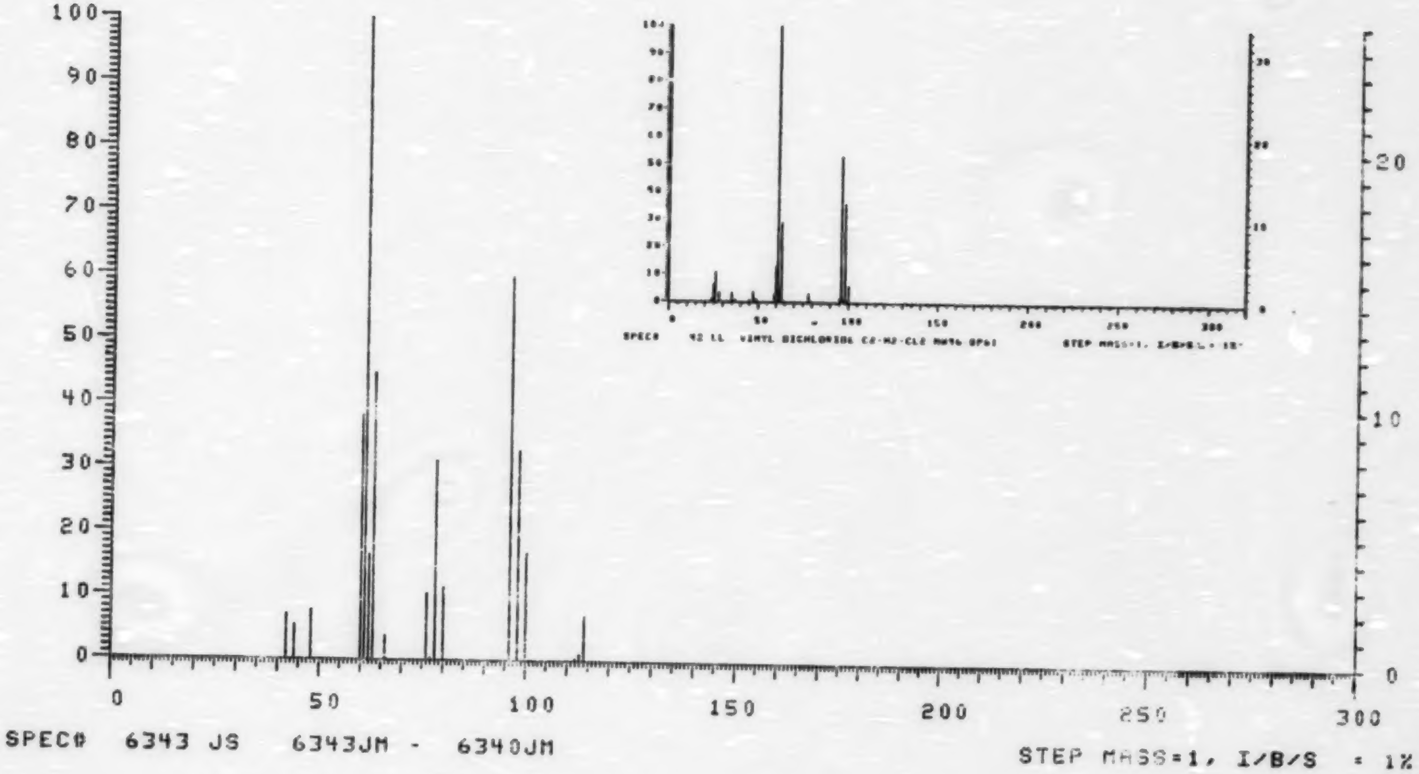

Figure 38. Mass spectrum of VDC in Dow Chemical, Michigan, Air Sample No. 3

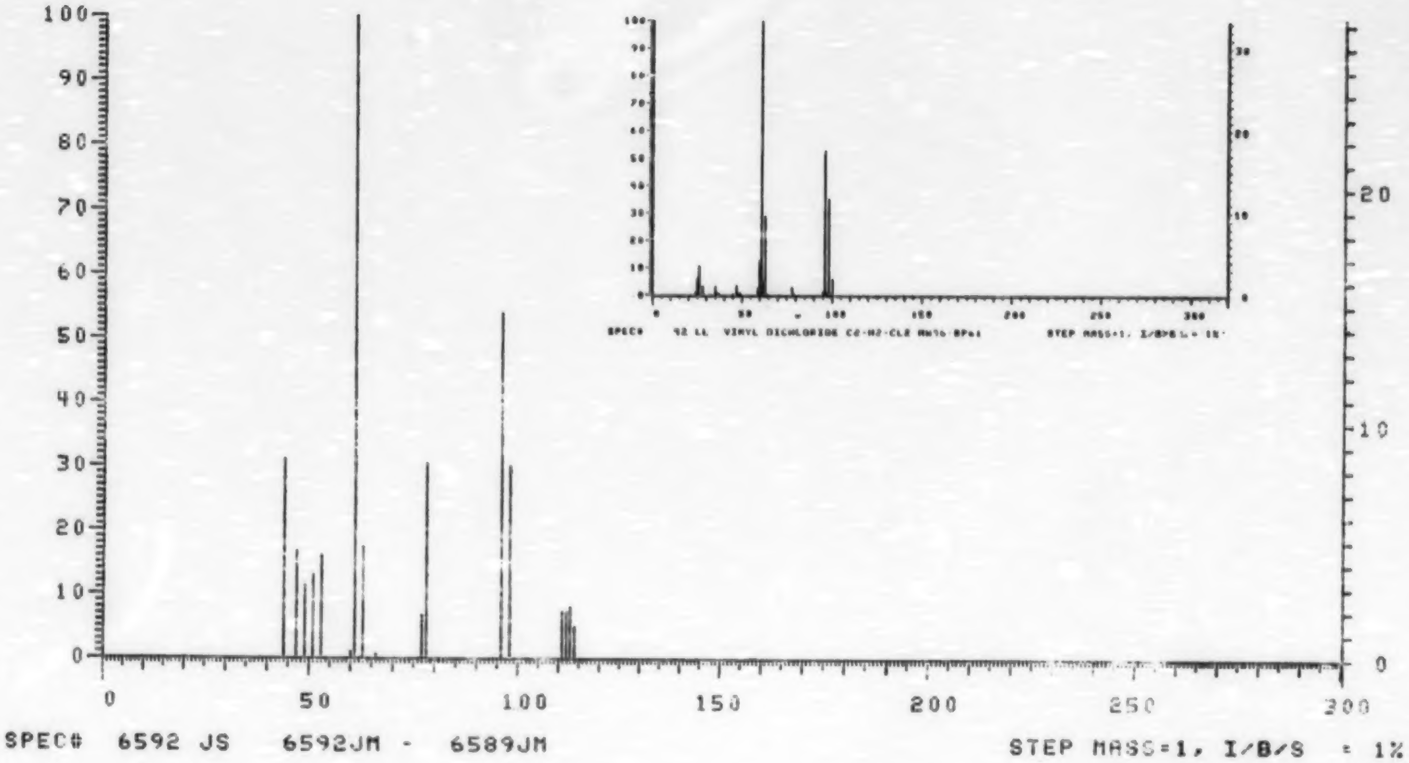

Figure 39. Mass spectrum of VDC in Dow Chemical, Michigan, Air Sample No. 11

The levels of VDC in the air, as micrograms per cubic meter, are given in Table 52 and are in Figure 35. Figure 40 shows a wind rose pattern depicting the wind behavior at the Tri City Airport, Freeland, Michigan, during the time when samples were being collected. The wind had a western component for over 80% of the sampling time and was evenly distributed from north-northwest to south-southwest. This indicates that Stations 3 and 11 were downwind of the plant and were the most likely stations where VDC would be detected. In fact, these were the most likely stations where VDC would be detected. In fact, these were the two locations where VDC was found; 25 $\mu g/m^3$ at Station 3, and 23 $\mu g/m^3$ at Station 11. The similarity in levels is in agreement with the wind patterns. No VDC was found at the upwind or crosswind stations.

Identification of Other Components - Most of the major peaks in the two Dow air Samples Nos. 3 and 11 were identified by EICPs. Upon close examination of the data, it was determined that one peak eluting immediately after *trans*-dichloroethylene in both of the samples remained unidentified. One subtracted spectrum was searched against the Cyphernetics file and identified as 2-methylpentane with a similarity index of 0.475. The peaks in the two Dow samples had the same retention time as the one of the peaks identified as a hexane in the Tennessee Eastman air sample. Tables 53 and 54 contain a complete listing of the compounds identified in air Samples Nos. 3 and 11, the basis of the identification, and whether the chemical is known to be a product or is heavily used by the company. All of the identified compounds in air Samples Nos. 3 and 11 are also noted on the sum plots shown in Figures 41 and 42, respectively.

Analysis of Water Samples

VDC Levels - The water samples collected at three locations along the Tittabawassee River were analyzed for VDC by GC using flame ionization detection. The analytical results are summarized in Table 55. No VDC was detected in any of the samples. The samples were analyzed by GC/MS in the MIS and VDC was detected in Sample W3. Identity was based up peak intensity ratios plus matching retention times. The peak intensity data are included in Table 55. The level of VDC was not quantified but was estimated to be between 0.1 and 1 ppb.

Identification of Other Components - Samples W1 and W3 were analyzed by GC/MS in an attempt to confirm VDC and to establish, if possible, the identity of any additional compounds present. The upstream Sample W1 showed four major peaks in the sum plot, while Sample W3 had about eight major and six minor additional peaks in its sum plot.

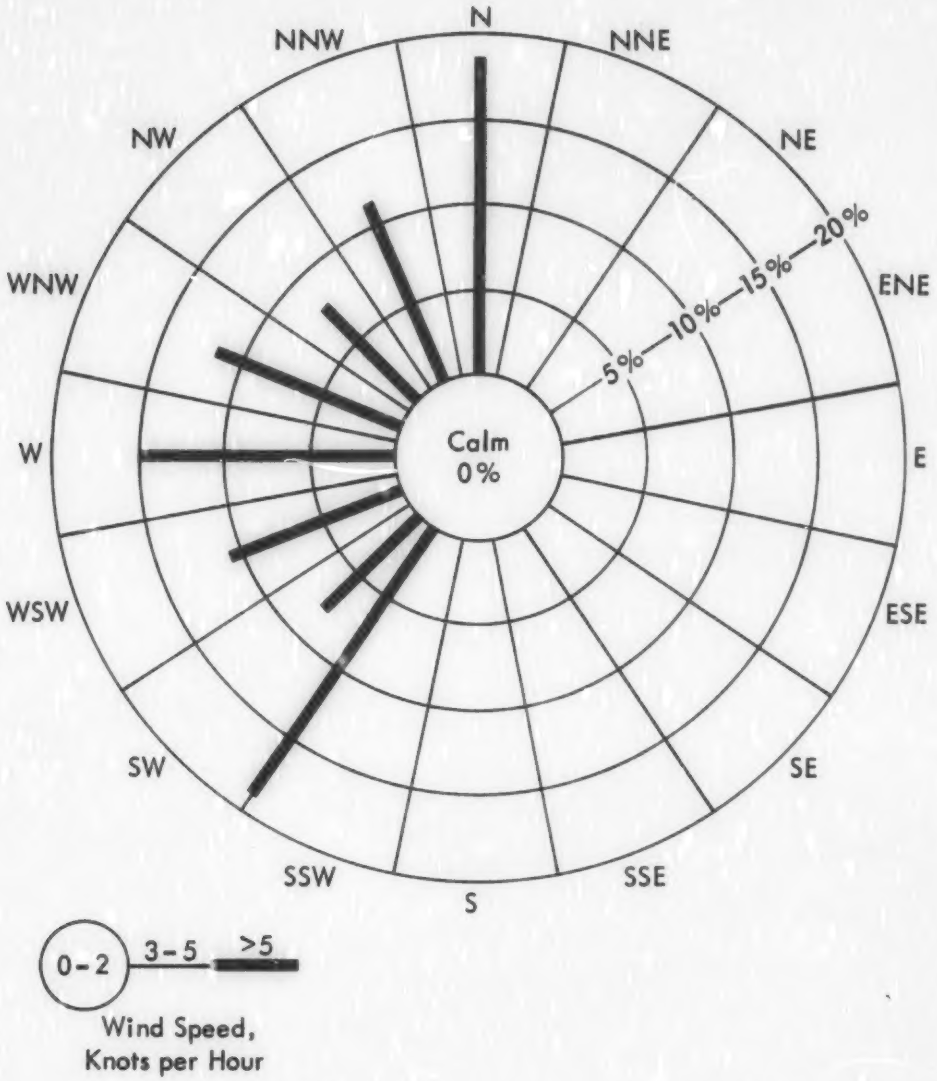

Figure 40. Wind Patterns During Sampling at Dow Chemical

Table 53. SUMMARY OF GC/MS ANALYSIS OF DOW AIR SAMPLE NO. 3

Compound	Basis of identification	m/e values	Intensity ratios	Spectrum number	Observed intensity ratios	Product or known use
Vinylidene chloride	SIP,[a] MAN[b]	61, 96, 98, 63	1.00:0.53:0.36:0.28	6343	1.00:0.60:0.33:0.44	Yes
trans-Dichloroethylene	SIP	61, 96, 98, 63	1.00:0.84:0.48:0.37	6359	1.0:0.8:0.5:0.3	No
2-Methylpentane	CYP[c]	-	-	6361	-	No
Methylene chloride	SIP	84, 86, 51, 88	1.00:0.71:0.37:0.09	6366	1.00:0.49:0.30:0.10	No
Methyl chloroform	SIP	97, 99, 117, 119	1.00:0.62:0.19:0.19	6396	1.0:0.7:0.2:0.1	No
Benzene	SIP	78, 52, 51, 50	1.00:0.17:0.15:0.12	6406	1.0:0.6:0.5:0.5	No
Toluene	SIP	91, 92, 65, 63	1.00:0.51:0.10:0.04	6437	1.0:0.54:0.17:0.08	No

---

[a] SIP = Selected ion plots.
[b] MAN = Manual interpretation of mass spectrum.
[c] CYP = Computer search of Cyphernetics file.

Table 54. SUMMARY OF GC/MS ANALYSIS OF DOW AIR SAMPLE NO. 11

Compound	Basis identification	m/e values	Intensity ratios	Spectrum number	Observed intensity ratios	Product or known use
Vinylidene chloride	SIP,a/ MANb/	61, 96, 98, 63	1.00:0.53:0.36:0.28	6592	1.00:0.54:0.30:0.18	Yes
trans-Dichloroethylene	SIP	61, 96, 98, 63	1.00:0.84:0.48:0.37	6608	1.0:0.5:0.3:0.2	No
2-Methylpentene	CYPc/	-	-	6611	-	No
Methylene chloride	SIP	84, 86, 51, 88	1.00:0.92:0.37:0.09	6616	1.00:0.75:0.60:0.10	No
Methyl chloroform	SIP (?)	97, 99, 117, 119	1.00:0.62:0.19:0.19	6647	1.0:0.5:0.2:-	No
Benzene	SIP	78, 52, 51, 50	1.00:0.17:0.15:0.12	6657	d/	No
Toluene	SIP	91, 92, 65, 63	1.00:0.51:0.10:0.04	6688	d/	No

a/ SIP = Selected ion plots.
b/ MAN = Manual interpretation of mass spectrum.
c/ CYP = Computer search of Cyphernetics file.
d/ One or more peaks saturated.

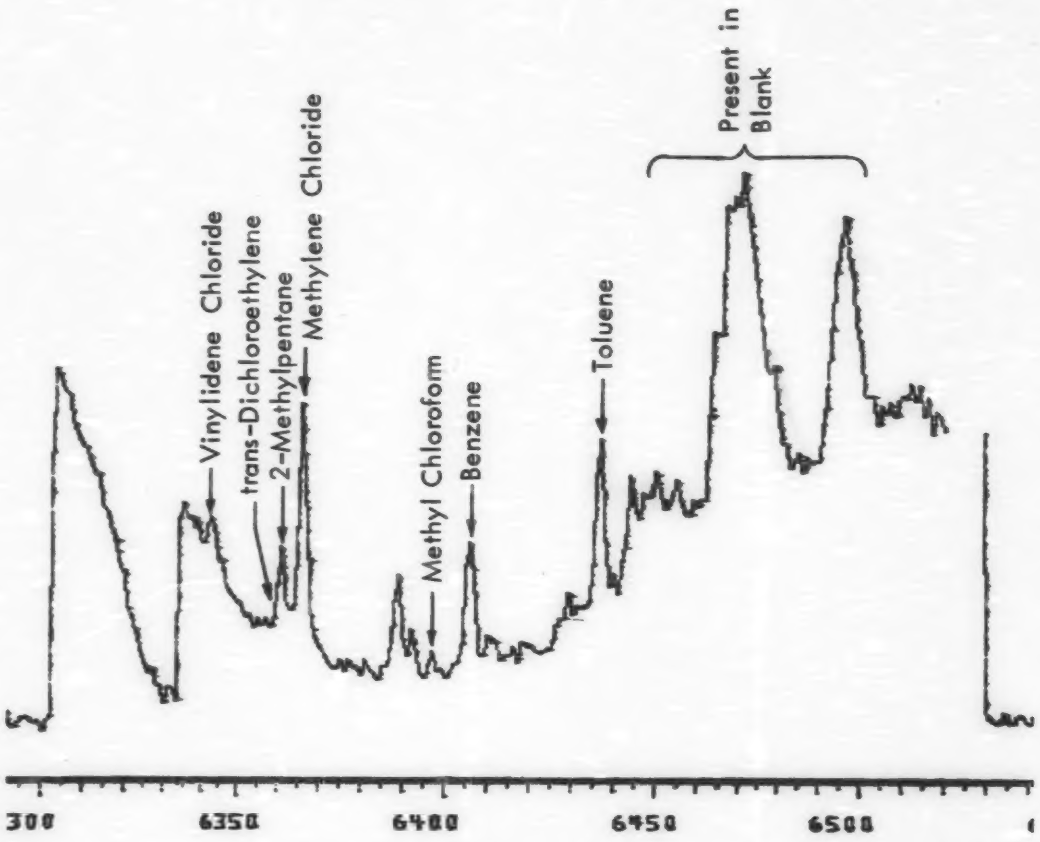

Figure 41. Sum plot of Dow Chemical, Michigan, Air Sample No. 3

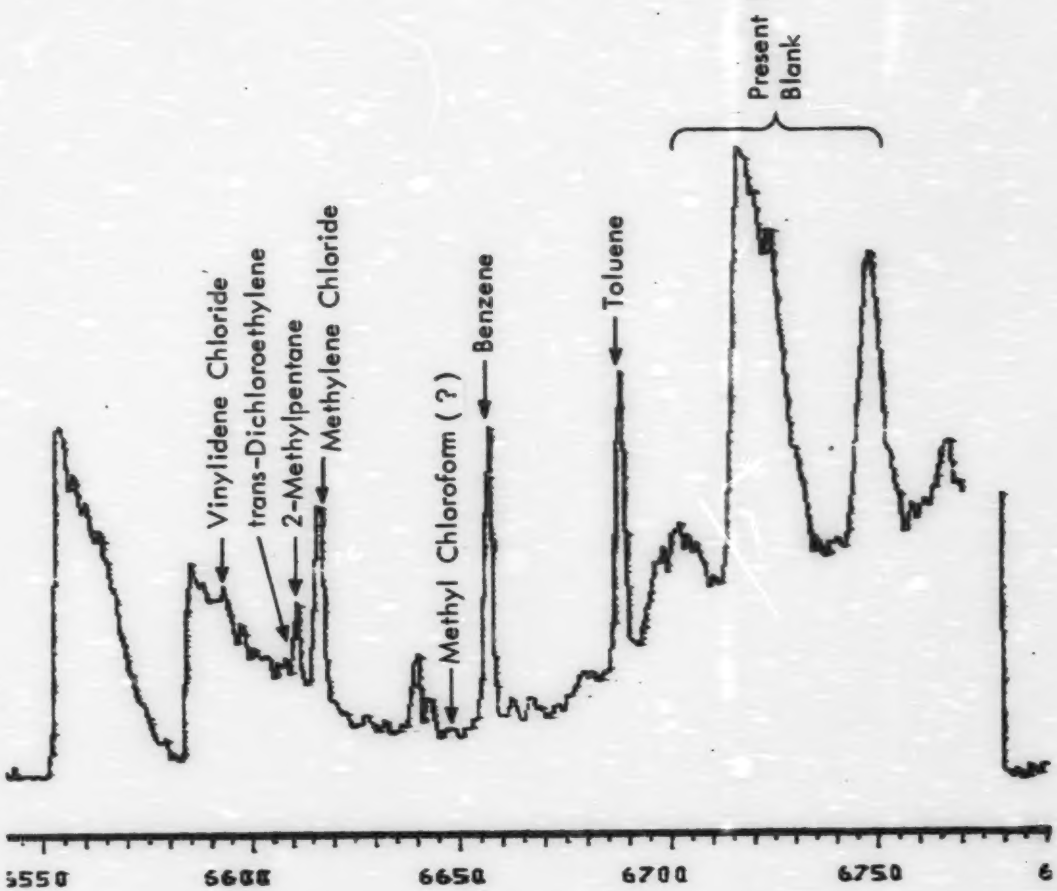

Figure 42. Sum plot of Dow Chemical, Michigan, Air Sample No. 11

Table 55. VDC CONCENTRATIONS IN WATER FROM DOW CHEMICAL, MIDLAND, MICHIGAN

Sample No.	Volume analyzed	VDC found GC-FID	 GC-MS-MIS (peak ratios)[a]	Level
W-1	10 ml	ND[b]	ND	ND
W-2	10 ml	ND	ND	ND
W-3	10 ml	ND	Yes (1.00:0.40:0.26:0.20)	< 1 ppb

---

[a] Peak intensities for m/e 61, 96, 98, 63 for standard were 1.00:0.36:0.21:0.14.

[b] ND = Not detected.

All of the compounds identified as being unique to Sample W3 are noted on the sum plot in Figure 43. Table 56 contains a complete listing of the identified compounds, the basis of the identification, and whether the compound is listed as a company product.

Dimethoxymethane was identified by searching mass spectrum No. 5497 against the Cyphernetics file. A similarity index of 0.654 was obtained. The authentic spectrum was retrieved from the Cyphernetics file and closely resembled the sample spectrum. Also, dimethoxymethane has a low enough boiling point (44°C) to elute at the observed retention time. While Dow does not list dimethoxymethane as a product, it does produce the structural isomer 2-methoxyethanol or methyl cellosolve.

Three brominated alkanes, bromochloromethane, dibromomethane, and 1-chloro-3-bromopropane were first identified by a manual study of the data. Authentic mass spectra for all three compounds were obtained from the Cyphernetics file and in all cases excellent agreement was obtained.

DRINKING WATER FROM FIVE U.S. CITIES

Field Sampling

The plan to collect drinking water samples from five major cities had been made by the previous project officer, Perry Brunner. The plan was to utilize local EPA or other personnel to collect and ship the water samples to MRI. Mr. Brunner made initial communication with the appropriate personnel to arrange for the collection of samples and establish the contact person for MRI. MRI then made initial contact with the individual who was to do the actual sampling. Table 57 lists the cities from which samples were collected as well as general information about the water supply.

Special water sampling kits were constructed at MRI and sent to the five cities. The kits contained 10, 25-ml screw cap vials that had been cleaned at 400°C. The vials were all fitted with Teflon® septa and five were labeled "Pre-chlorination" and five were labeled "Post-chlorination." The kit was actually a polystyrene shipping carton that had been modified to hold the 10 vials and two ice packs as well. Detailing sampling and shipping instructions accompanied each sampling kit. The kits were all shipped on March 29. Table 57 lists the samples which were collected and the date on which they arrived at MRI.

Analysis of Water Samples

The pre- and post-chlorinated drinking water from four of the five cities was analyzed for VDC using the previously established GC/MS/MIS procedure.

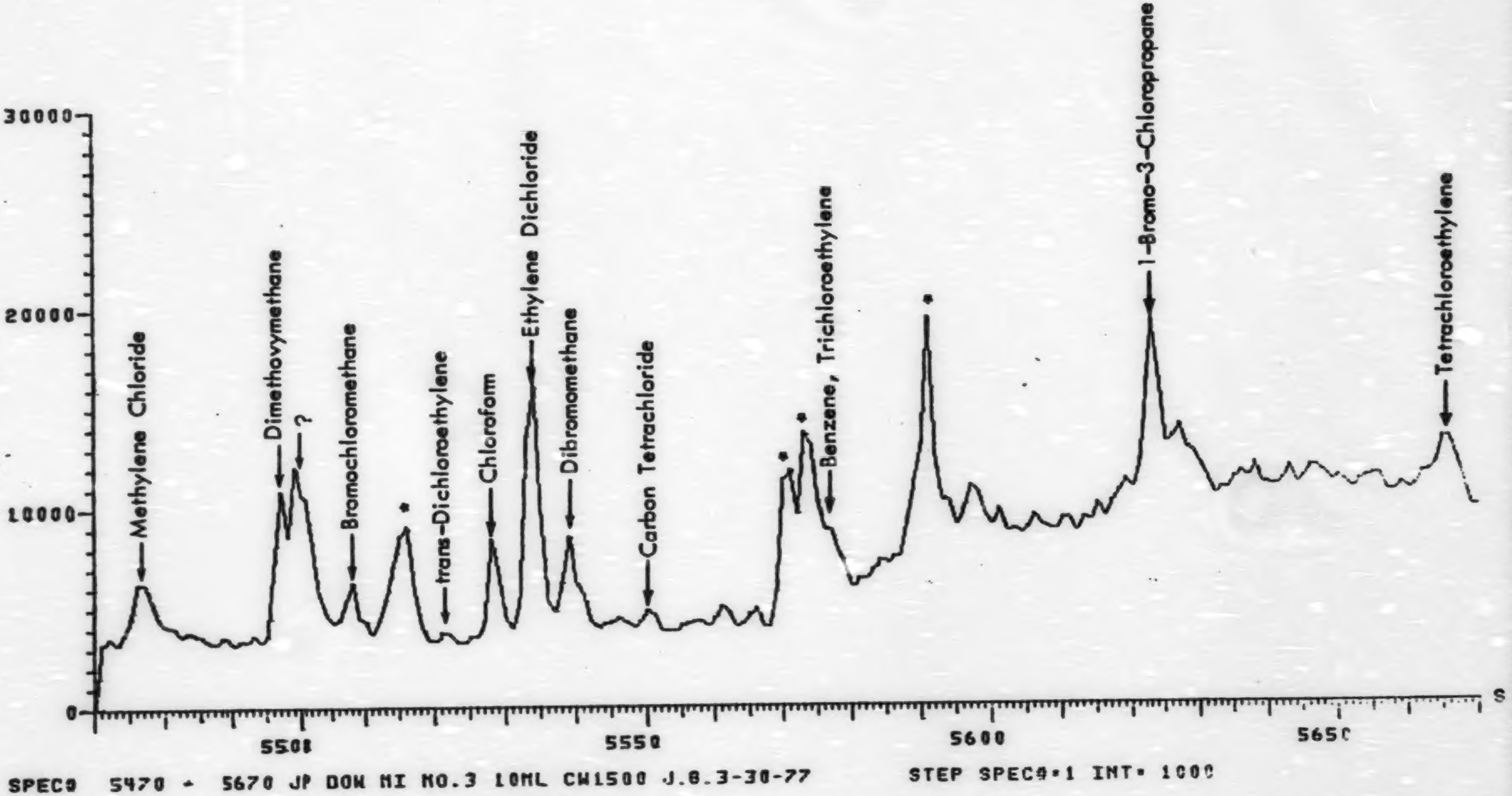

Figure 43. Sum plot of Dow Chemical, Michigan, Water Sample W-3
* Peaks found in upstream sample

Table 56. SUMMARY OF GC/MS ANALYSIS OF DOW WATER SAMPLE W-3

Compound	Basis of identification	m/e values	Intensity ratios	Spectrum number	Observed intensity ratios	Product
Methylene chloride	SIP[a]	84, 86, 51, 88	1.00:0.71:0.34:0.10	5476	1.00:0.77:0.45:0.15	No
Vinylidene chloride	MIS[b]	61, 96, 98, 63	1.00:0.36:0.21:0.14	~ 5499	1.00:0.40:0.26:0.20	Yes[c]
Dimethoxymethane	CYP[d]	-	-	5497	-	[e]
Bromochloromethane	MAN, SP[f]	-	-	5508	-	Yes
trans-Dichloroethylene	SIP	61, 96, 98, 63	1.00:0.84:0.48:0.37	5522	1.0:0.6:0.6:0.4	No
Chloroform	SIP	83, 85, 47, 87	1.00:0.55:0.14:0.07	5528	1.00:0.42:0.17:0.13	No
Ethylene dichloride	SIP	62, 64, 98, 100	1.00:0.31:0.08:0.06	5534	1.0:0.6:0.2:0.1[g]	No
Dibromomethane	MAN, SP	-	-	5539	-	Yes
Carbon tetrachloride	SIP	119, 117, 121, 82	1.00:0.98:0.25:0.13	5550	1.0:0.8:0.1:0.1	No
Benzene	SIP	78, 52, 51, 50	1.00:0.17:0.12:0.10	5576	1.00:0.12:0.14:0.12	No
Trichloroethylene	SIP	130, 132, 95, 97	1.00:0.94:0.86:0.59	5577	1.00:1.00:1.67:0.67	No
1-Chloro-3-bromopropane	MAN, SP	-	-	5623	-	No
Tetrachloroethylene	SIP	164, 166, 129, 131	1.00:0.78:0.75:0.85	5665	1.00:0.80:0.80:0.95	No

[a] SIP = Selected ion plots.
[b] MIS = Multiple ion scan.
[c] VDC is used as a starting material.
[d] CYP = Computer search of Cyphernetics file.
[e] Dow produces the structural isomer methyl cellosolve.
[f] Comparison to authentic spectrum.
[g] m/e 62 peak saturated.

Table 57. DRINKING WATER SAMPLES FROM FIVE U.S. CITIES

City	Treatment plant	Contact	Type of supply	Type of raw water	Results of NORS study[a]	Samples collected	Date received
Cincinnati, Ohio	[b]	J. W. Oehler	Surface	Industrial waste	[c]	5 at pre-chlorination 5 at post-chlorination	4/5/77
Lawrence, Massachusettes	[b]	T. Murphy	Surface	Industrial waste	[c]	5 at pre-chlorination 5 at post-chlorination	4/14/77
Miami, Florida	Preston	D. H. Waddell	Ground	Natural waste	0.1 µg/	5 at pre-chlorination 5 at post-chlorination	4/12/77
Waterford, New York	[b]	T. DeGaetano	Ground	[d]	[d]	5 at pre-chlorination 5 at post-chlorination	4/18/77
Philadelphia, Pennsylvania	Torresdale	B. Blankenship	Surface	Municipal waste	< 0.1 µg/	5 at pre-chlorination 5 at post-chlorination	4/7/77

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[a] "Preliminary Assessment of Suspected Carcinogens in Drinking Water: Report to Congress," EPA, Washington, D.C.

[b] No specific treatment plant designated.

[c] VDC detected but not quantified.

[d] Unable to determine.

The sample from Waterford, New York, did not arrive in time to be analyzed on the scheduled analysis date, April 15. The results of the analyses are given in Table 58. No VDC was found in any of the samples except the pre- (90.59 μg/liter) and post-chlorination (0.45 μg/liter) samples from the Preston plant, Miami, Florida. The MIS plots for the two Miami samples and the 1 ng VDC standard are shown in Figure 44. Confirmation of VDC is based upon matching retention times and matching peak intensity ratio. The intensity ratio data are footnoted in Table 46. The estimated detection limit, using a 10-ml sample, was 0.005 ppb.

SOLID FINAL PRODUCTS

Field Sampling

Samples of solid final products manufactured from VDC were requested from about 30 companies. The companies were selected to be representative of total industrial use of VDC. The samples described in Table 59 either received from the manufacturer or purchased locally.

Analysis of Solid Products

Four types of commercial PVDC products were analyzed for residual VDC monomer, and the results are summarized in Table 60. VDC was detected in the two samples of Saran Wrap but not in the monofilaments, modacrylic fibers or the meat packaging film. The Saran Wrap, presumably produced in 1974, was found to contain 41 ppm VDC compared to 58 ppm found in the same sample in October 1976. The Saran Wrap, presumably produced in 1976, was found to contain only 4.9 ppm VDC. This is consistent with the recent statement by Dow Chemical that its Saran Wrap contains "no more than 10 ppm of unreacted monomers."[4]

The estimated detection limit for the procedure was 0.005 ppm. Consequently the monofilaments, the modacrylic fiber, and the meat packaging film were judged to contain less than 0.005 ppm VDC.

Table 58. VDC CONCENTRATIONS IN DRINKING WATER FROM FOUR U.S. CITIES

Sample	Sample size (ml)	VDC found (ng)	VDC (μg/ℓ)
Cincinnati pre-chlorination	10	ND	ND
Cincinnati post-chlorination	10	ND	ND
Lawrence pre-chlorination	10	ND	ND
Lawrence post-chlorination	10	ND	ND
Miami pre-chlorination	10	0.59[a]	0.059
Miami post-chlorination	10	0.45[a]	0.045
Waterford pre-chlorination	10	b/	b/
Waterford post-chlorination	10	b/	b/
Philadelphia pre-chlorination	10	ND	ND
Philadelphia post-chlorination	10	ND	ND

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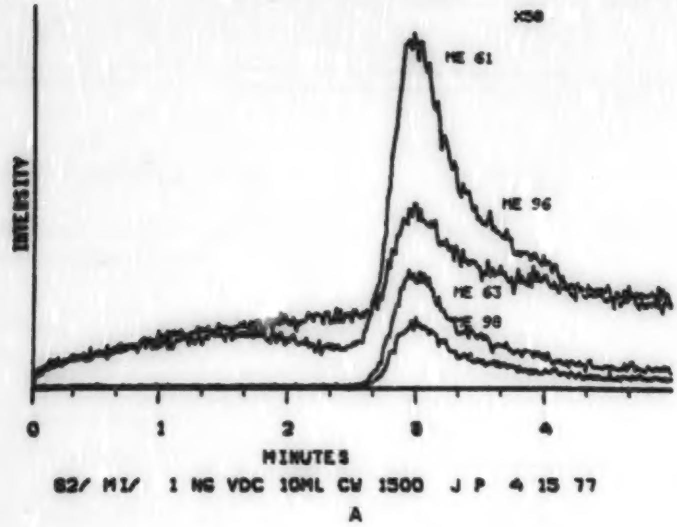
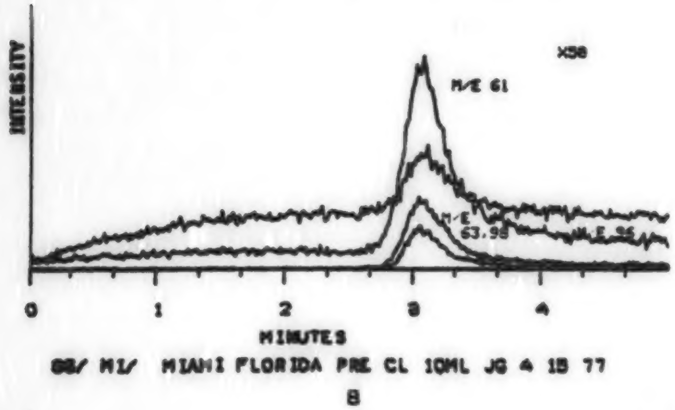
a/ The measured intensity ratios for the ions 61, 63, 96, and 98 were 1.00:0.39:0.33:0.20 for standard VDC; 1.00:0.39:0.33:0.22 for Miami pre-chlorination; and 1.00:0.36:0.31:0.21 for Miami post-chlorination.

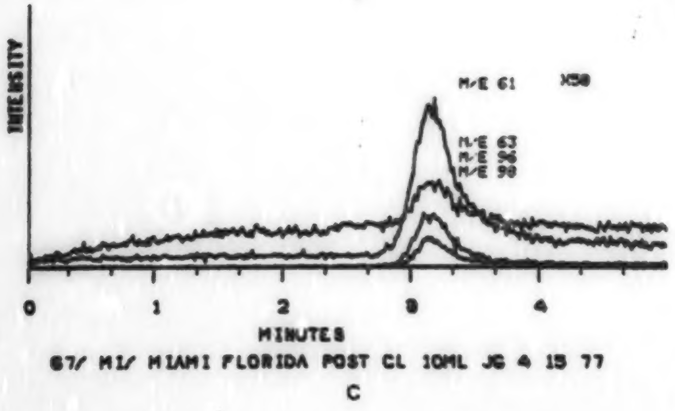
b/ Sample not received in time for scheduled analysis.



(a) One nanogram standard



(b) Miami, Florida, pre-chlorinated drinking water



(c) Miami, Florida, post-chlorinated drinking water

Figure 44. Multiple ion scan of VDC in drinking waters

Table 59. SOLID FINAL PRODUCT SAMPLES

Sample description	Source	Date received
Saran Wrap, carton coded 2474	Purchased locally	10/76
Saran Wrap, carton coded 060376	Purchased locally	3/77
Amtech monofilaments, produced from Dow B-Copolymer	Supplied by manufacturer	11/3/76
Monsanto modacrylic fiber, 1 lb	Supplied by manufacturer	11/24/76
Oscar Meyer, films A, B, and C	Supplied by manufacturer	12/9/76

Table 60. VDC CONCENTRATIONS IN SOLID PRODUCTS

Sample	Source	Sample size range (g)	ppm
Saran Wrap (carton coded 2474)	Local grocery store	1.96-2.43	41[a] (58)[b]
Saran Wrap (carton coded 060376)	Local grocery store	1.83-2.11	4.9[a]
Amtech monofilaments	Manufacturer	0.20-1.29	ND[c]
Monsanto modacrylic fiber	Manufacturer	1.00-1.42	ND[a]
Oscar Meyer Film A	Manufacturer	2.40-3.03	ND[d]
Oscar Meyer Film B	Manufacturer	3.98-4.27	ND[d]
Oscar Meyer Film C	Manufacturer	3.47-3.71	ND[d]

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[a] Average of three samples.

[b] Analyzed October 1976.

[c] Five samples analyzed in duplicate.

[d] Analyzed in duplicate.

REFERENCES

1. "Sampling and Analysis of Selected Toxic Substances, Task IV, Ethylene Dibromide, EPA 560/6- 76-021.

2. Personal communication, John Cobler, Dow Chemical, USA, Midland, Michigan.

3. "Vinylidene Chloride Monomer Emissions from the Monomer, Polymer, and Polymer Processing Industries," A. D. Little, Inc., EPA Contract No. 68-02-1332, Task Order No. 13, April 1976.

4. Chem. and Eng. News, 21, March 17, 1977.